D E C L A R A T I O N

I, SHINICHI USUI, a Japanese Patent Attorney registered No.9694, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No.2002-310250 filed on October 24, 2002 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 30th day of April, 2008

SHINICHI USUI

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Application Number: Japanese Patent Application
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Applicant(s): CANON KABUSHIKI KAISHA

November 27, 2003

Commissioner,
Patent Office Yasuo IMAI

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Applicant's Information

Identification No.	[000001007]
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(Reason of Change)	New Registration
Address:	3-30-2, Shimomaruko, Ohta-ku, Tokyo
Name:	CANON KABUSHIKI KAISHA

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[Date] October 24, 2002

[Addressed to] Commissioner of the Patent Office

[International Classification] C12P 7/62
C08G 63/06

[Title of the Invention] NOVEL POLYHYDROXY ALKANOATE COPOLYMER INCLUDING WITHIN MOLECULE UNIT HAVING VINYL GROUP OR CARBOXYL GROUP IN SIDE CHAIN, AND PRODUCING METHOD THEREFOR

[Number of the Claims] 35

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Takashi KENMOKU

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Chieko MIHARA

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Tatsuki FUKUI

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Tetsuya YANO

[Applicant]

[Identification No.] 000001007

[Domicile or Residence]	c/o Canon Kabushiki Kaisha 30-2, 3-chome, Shimomaruko, Ohta-ku, Tokyo
[Name]	CANON KABUSHIKI KAISHA

[Attorney]

[Identification No.]	100088328
[Patent Attorney]	
[Name]	Nobuyuki KANEDA
[Telephone Number]	03-3585-1882

[Elected Attorney]

[Identification No.]	100106297
[Patent Attorney]	
[Name]	Katsuhiro ITO

[Elected Attorney]

[Identification No.]	100106138
[Patent Attorney]	
[Name]	Masayuki ISHIBASHI

[Indication of Official Fee]

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[List of Filed Materials]

[Material]	Specification	1
[Material]	Drawings	1
[Material]	Abstract	1
[Proof requirement]	necessary	

CFO17653WOUS

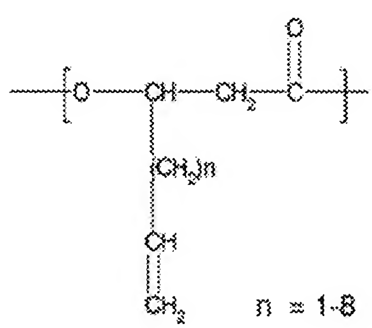
[Name of the Document] Specification

[Title of the Invention] Novel Polyhydroxy Alkanoate Copolymer including within Molecule Unit Having Vinyl Group or Carboxyl Group in Side Chain, and Producing Method Therefor

[Claim(s)]

[Claim 1] A polyhydroxy alkanoate copolymer characterized in including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

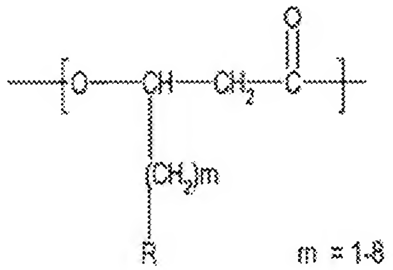
[Chemical Formula 1]



(1)

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

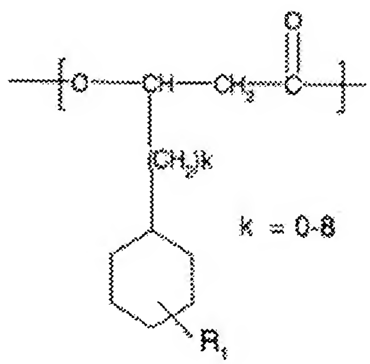
[Chemical Formula 2]



(2)

in which m represents an integer selected within a range indicated in the chemical formula; R represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit;

[Chemical Formula 3]



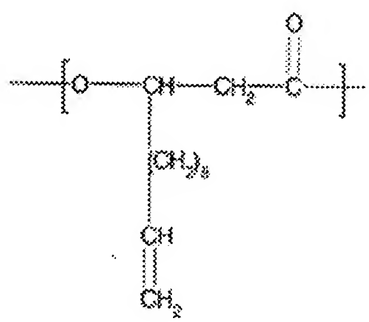
(3)

in which R_1 being a substituent on a cyclohexyl group represents a hydrogen atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit.

[Claim 2] The polyhydroxy alkanoate copolymer

according to claim 1, wherein the 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) is any one of a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

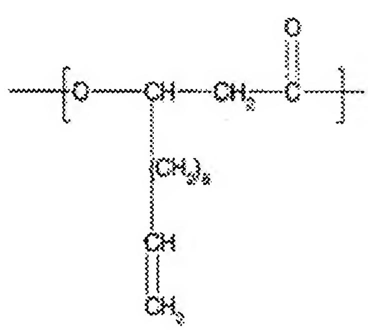
[Chemical Formula 4]



(4)

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

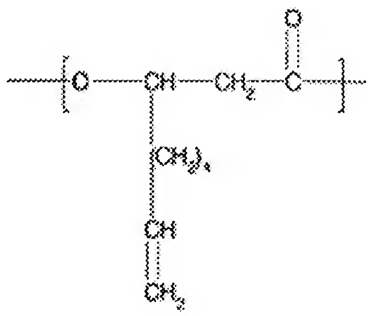
[Chemical Formula 5]



(5)

a 3-hydroxy-8-nonenoic acid unit represented by a chemical formula (6): and

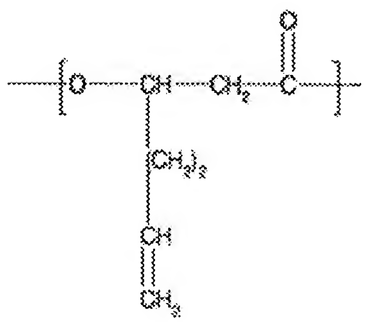
[Chemical Formula 6]



(6)

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7)

[Chemical Formula 7]

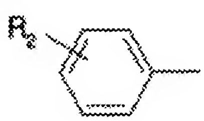


(7).

[Claim 3] The polyhydroxy alkanoate copolymer according to claim 1 or 2, wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from the group consisting of chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (8):

[Chemical Formula 8]



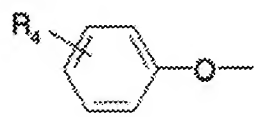
(8)

represents a group of non-substituted or substituted

phenyl groups in which R_2, a substituent on an aromatic ring and represents an H atom, represents a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a $COOR_3$ group (R_3 represents an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 9]

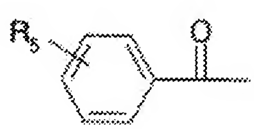


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 10]



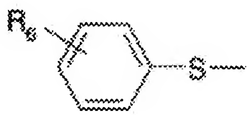
(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on

an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11)

[Chemical Formula 11]

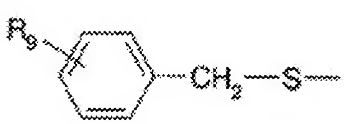


(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 12]



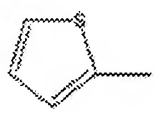
(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a

substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 13]

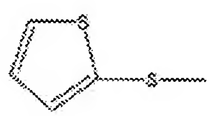


(13)

represents a 2-thienyl group;

the chemical formula (14)

[Chemical Formula 14]

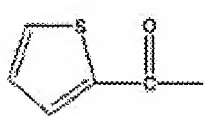


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 15]

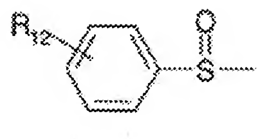


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 16]

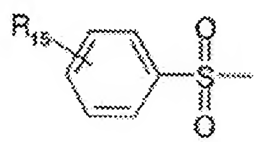


(16)

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 17]



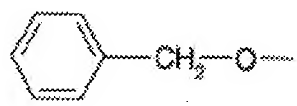
(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be

the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 18]

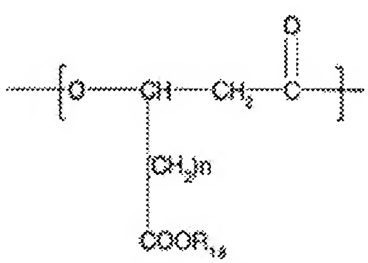


(18)

represents a (phenylmethyl)oxy group.

[Claim 4] A polyhydroxy alkanoate copolymer characterized in including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

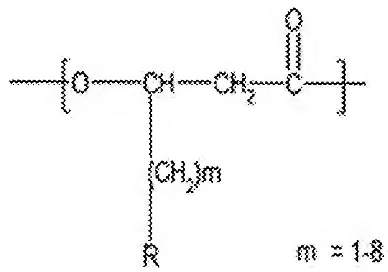
[Chemical Formula 19]



n = 1-8 (19)

in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom or a K atom: and in case plural units are present, n and R_{18} may be the same or different for each unit;

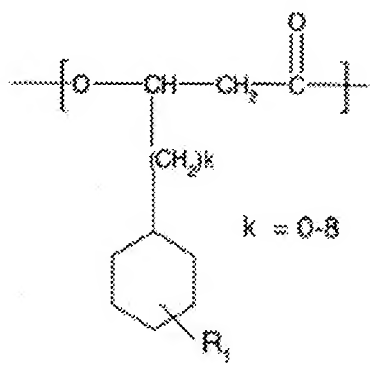
[Chemical Formula 20]



(2)

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit; and

[Chemical Formula 21]

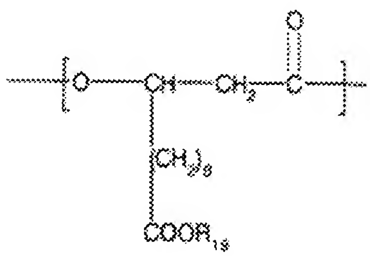


(3)

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit.

[Claim 5] The polyhydroxy alkanoate copolymer according to claim 4, wherein the 3-hydroxy-ω-carboxyalkanoic acid unit represented by the chemical formula (19) is any one of a 3-hydroxy-11-carbonylundecanoic acid unit represented by a chemical formula (20):

[Chemical Formula 22]

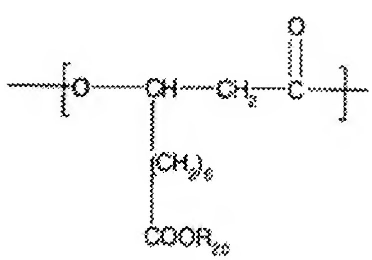


(20)

(R_{19} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{19} may be the same or different for each unit),

a 3-hydroxy-9-carboxynonanoic acid unit represented by a chemical formula (21):

[Chemical Formula 23]

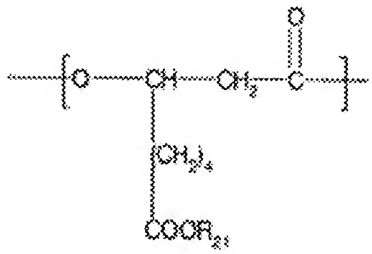


(21)

(R_{20} represents an H atom, a Na atom or a K atom and in case plural units are present; and R_{20} may be the same or different for each unit),

a 3-hydroxy-7-carboxyheptanoic acid unit represented by a chemical formula (22):

[Chemical Formula 24]

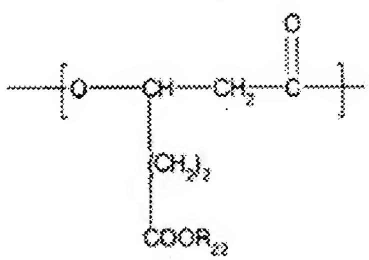


(22)

(R_{21} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{21} may be the same or different for each unit), and

a 3-hydroxy-5-carboxyvaleric acid unit represented by a chemical formula (23):

[Chemical Formula 25]



(23)

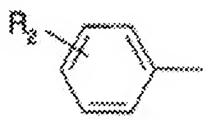
(R_{22} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{22} may be the same or different for each unit).

[Claim 6] The polyhydroxy alkanoate copolymer according to claim 4 or 5, wherein R in the chemical formula (2), represents a residue having a phenyl structure or a thienyl structure selected from chemical formulas (8), (9), (10), (11), (12), (13), (14), (15),

(16), (17), and (18):

the chemical formula (8):

[Chemical Formula 26]

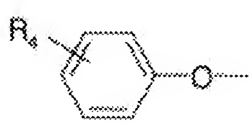


(8)

represents a group of non-substituted or substituted phenyl groups in which R_2 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a $COOR_3$ group (R_3 representing an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 27]

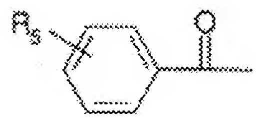


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 28]

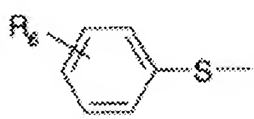


(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 29]

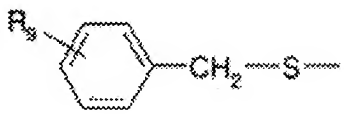


(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 30]

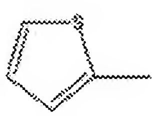


(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 31]

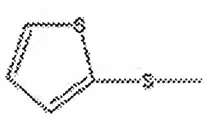


(13)

represents a 2-thienyl group;

the chemical formula (14):

[Chemical Formula 32]

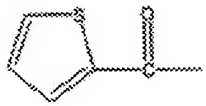


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 33]

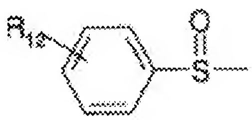


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 34]

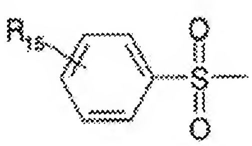


(16)

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 35]



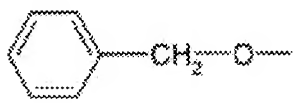
(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 36]



(18)

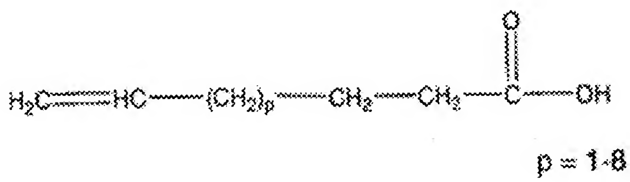
represents a (phenylmethyl)oxy group.

[Claim 7] The polyhydroxy alkanoate copolymer according to any one of claims 1 to 6, wherein a number-averaged molecular weight is within a range from 1000 to 1000000.

[Claim 8] A method for producing a polyhydroxy alkanoate copolymer characterized in including a biosynthesis by a microorganism having an ability of producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, from at least an

ω-alkenoic acid represented by a chemical formula (24) and at least a compound represented by a chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by a chemical formula (26) as starting materials:

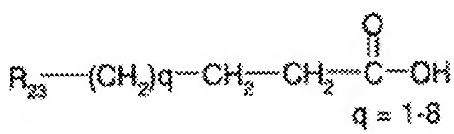
[Chemical Formula 37]



(24)

in which p represents an integer selected within a range indicated in the chemical formula;

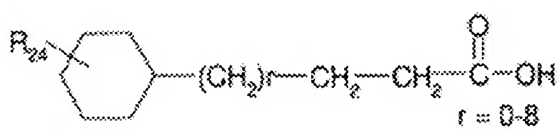
[Chemical Formula 38]



(25)

in which q represents an integer selected within a range indicated in the chemical formula; and R_{23} includes a residue having a phenyl structure or a thienyl structure;

[Chemical Formula 39]

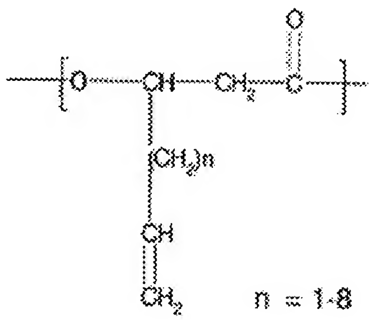


(26)

in which R_{24} represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group,

a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula;

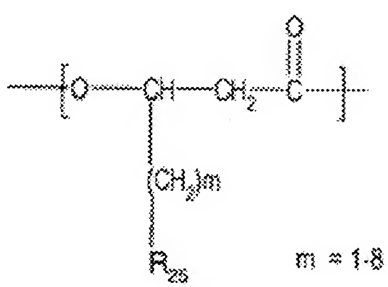
[Chemical Formula 40]



(1)

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

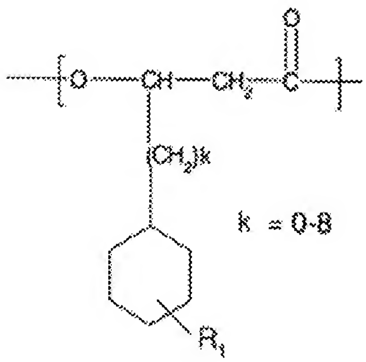
[Chemical Formula 41]



(27)

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit; and

[Chemical Formula 42]

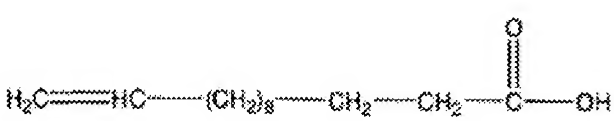


(3)

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

[Claim 9] The method for producing a polyhydroxy alkanoate copolymer according to claim 8, wherein the ω-alkenoic acid represented by the chemical formula (24) is a 12-tridecenoic acid represented by a chemical formula (28): or

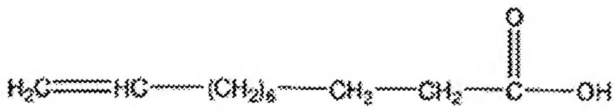
[Chemical Formula 43]



(28)

a 10-undecenoic acid represented by a chemical formula (29): or

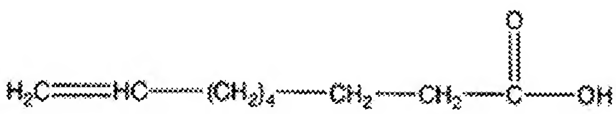
[Chemical Formula 44]



(29)

a 8-nonenoic acid unit represented by a chemical formula (30):

[Chemical Formula 45]



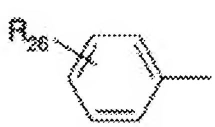
(30)

.

[Claim 10] The method for producing a polyhydroxy alkanoate copolymer according to claim 8 or 9, wherein R_{23} in the chemical formula (25) and R_{25} in the chemical formula (27), each represents a residue having a phenyl structure or a thienyl structure, are selected from chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (31):

[Chemical formula 46]



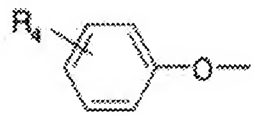
(31)

represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present,

R_{26} may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 47]

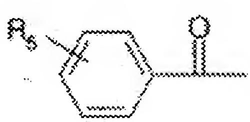


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 48]

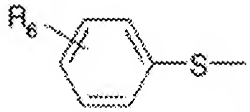


(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 49]

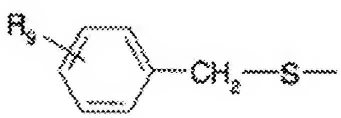


(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 50]



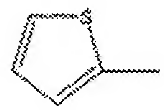
(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a (CH3)$_3$-C group; and in case plural units are present,

R_9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 51]

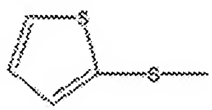


(13)

represents a 2-thienyl group;

the chemical formula (14):

[Chemical Formula 52]

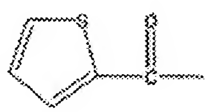


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 53]

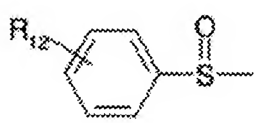


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 54]



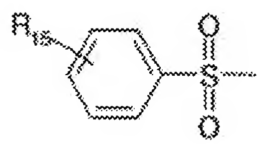
(16)

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H,

Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

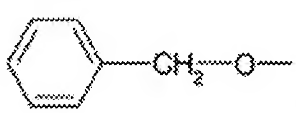
[Chemical Formula 55]


(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 56]


(18)

represents a (phenylmethyl)oxy group.

[Claim 11] The method for producing a polyhydroxy

alkanoate copolymer according to any one of claims 8 to 10, wherein said microorganism is cultured in a culture medium including at least a ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26).

[Claim 12] The method for producing a polyhydroxy alkanoate copolymer according to claim 11, wherein said microorganism is cultured in a culture medium including, in addition to at least an ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar, a linear alkanoic acid with 4 to 12 carbon atoms or a salt thereof.

[Claim 13] The method for producing a polyhydroxy alkanoate copolymer according to claim 12, wherein for culturing said organism, the peptide to be added to the culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of piruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; amino acid or salt

thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid, aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[Claim 14] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 8 to 13, characterized in including a step of culturing said microorganism in a culture medium including at least an ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by the chemical formula (26), and recovering a polyhydroxy alkanoate copolymer including simultaneously at least a 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) and a 3-hydroxy-ω-alkanoic acid unit represented by the chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by said microorganism, from cells of the microorganism.

[Claim 15] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 8 to 14, wherein said microorganism is a microorganism

belonging to Pseudomonas genus.

[Claim 16] The method for producing a polyhydroxy alkanoate copolymer according to claim 15, wherein said microorganism is at least one of Pseudomonas cichorii YN2 strain (FERM BP-7375), Pseudomonas cichorii H45 strain (FERM BP-7374), Pseudomonas jessenii P161 (FERM BP-7376) and `Pseudomonas putida P91 (FERM BP-7373).

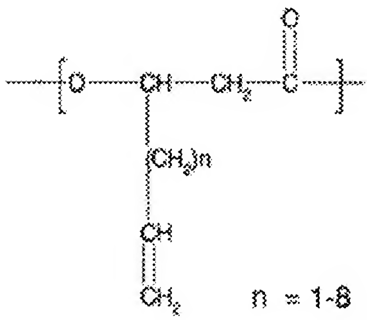
[Claim 17] A method for producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule comprising the steps of: preparing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule as a starting material, and

oxidizing and cleaving a double bond portion in the polyhydroxy alkanoate represented in the chemical formula (1) thereby

generating a polyhydroxy alkanoate copolymer

including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

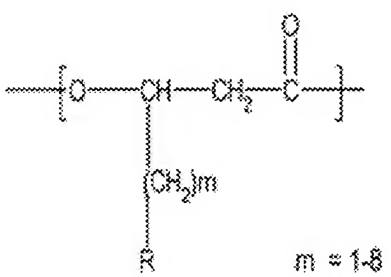
[Chemical Formula 57]



(1)

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[Chemical Formula 58]

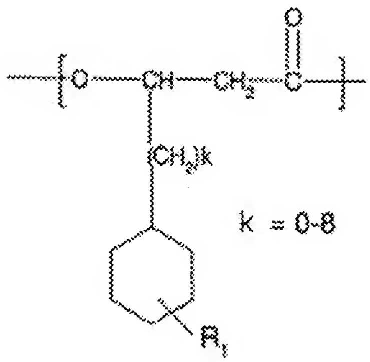


(2)

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure and a thienyl

structure; and in case plural units are present, m and R may be the same or different for each unit;

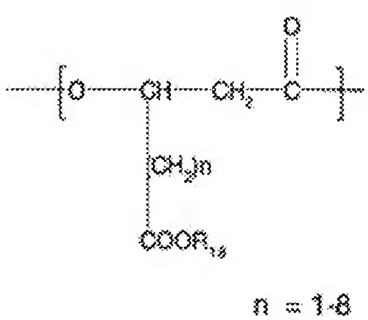
[Chemical Formula 59]



(3)

in which R_1 represents a substituent on a cyclohexyl group selected from an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, and a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit; and

[Chemical Formula 60]



(19)

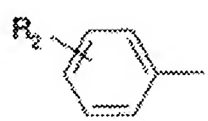
in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents

an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

[Claim 18] The method for producing a polyhydroxy alkanoate copolymer according to claim 17, wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (8):

[Chemical Formula 61]

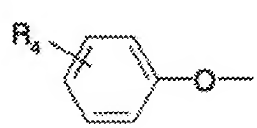


(8)

represents a group of non-substituted or substituted phenyl groups in which R_2 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH{=}CH_2$ group, a $COOR_3$ group (R_3 representing an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 62]

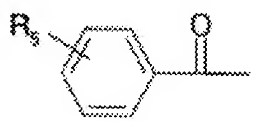


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 63]

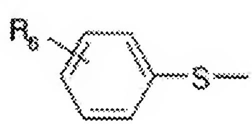


(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 64]



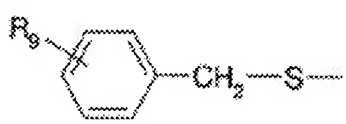
(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 65]

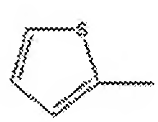


(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 66]

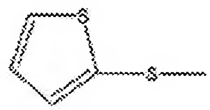


(13)

represents a 2-thienyl group;

the chemical formula (14):

[Chemical Formula 67]

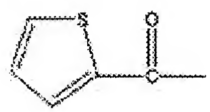


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 68]

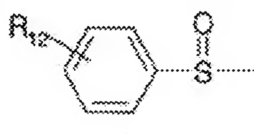


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 69]

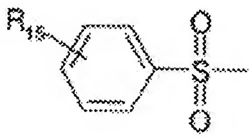


(16)

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH3 and C2H5; and R14 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 70]

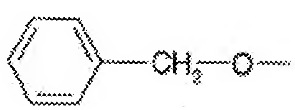


(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit;

the chemical formula (18):

[Chemical Formula 71]



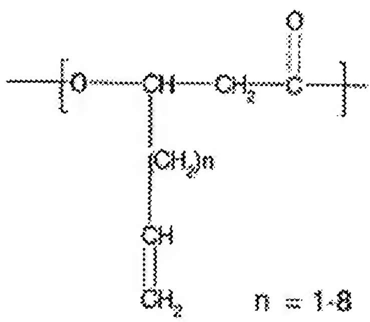
(18)

represents a (phenylmethyl)oxy group.

[Claim 19] The method according to claim 17 or 18, wherein said starting material polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula

(27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, is produced by a method according to any one of claims 8 to 16;

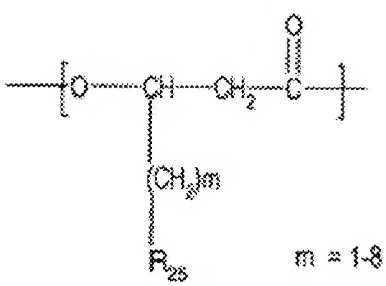
[Chemical Formula 72]



(1)

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

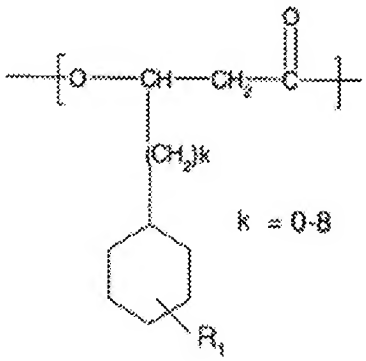
[Chemical Formula 73]



(27)

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit; and

[Chemical Formula 74]



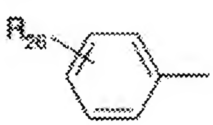
(3)

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

[Claim 20] The method for producing a polyhydroxy alkanoate copolymer according to claim 19, wherein R_{25} in the chemical formula (27), representing a residue having a phenyl structure or a thienyl structure, is at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (31):

[Chemical Formula 75]



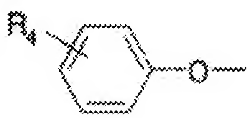
(31)

represents a group of substituted or non-substituted

phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 76]

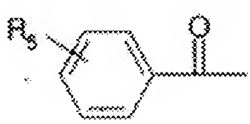


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 77]



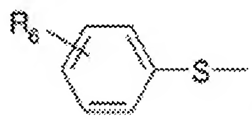
(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;

and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 78]

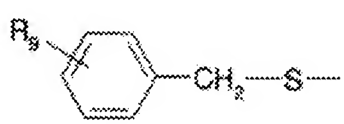


(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 79]



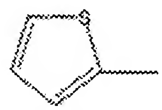
(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H,

Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H^7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 80]

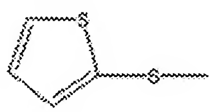


(13)

represents a 2-thienyl group;

the chemical formula (14):

[Chemical Formula 81]

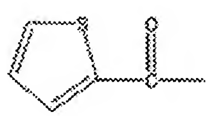


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 82]

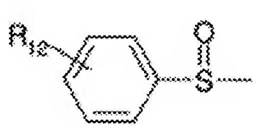


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 83]



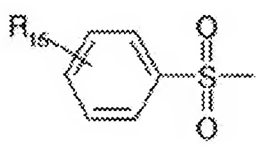
(16)

represents a group of substituted or non-substituted

phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 84]

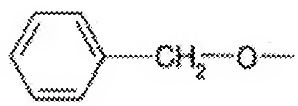


(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 85]

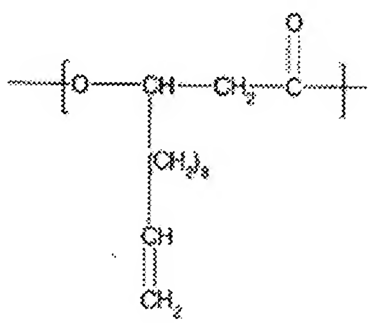


(18)

represents a (phenylmethyl)oxy group.

[Claim 21] The polyhydroxy alkanoate copolymer according to any one of claims 17 to 20, wherein the 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) is any one of a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

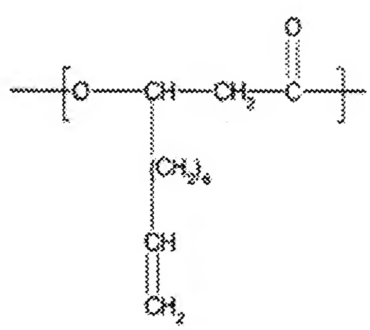
[Chemical Formula 86]



(4)

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

[Chemical Formula 87]

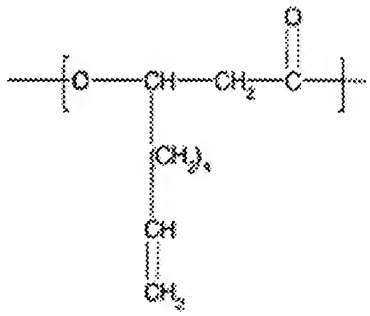


(5)

a 3-hydroxy-8-nonenoic acid unit represented by a

chemical formula (6): and

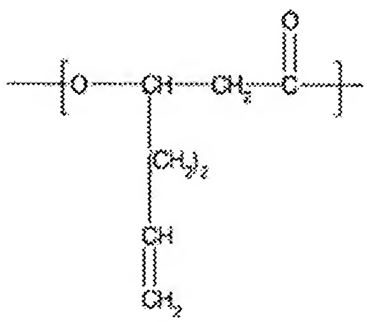
[Chemical Formula 88]



(6)

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7)

[Chemical Formula 89]



(7)

.

[Claim 22] The producing method according to any one of claims 17 to 21, wherein said oxidation and cleavage reaction is carried out with an oxidant selected from a group consisting of a permanganate, a bichromate and a periodate.

[Claim 23] The producing method according to claim 22, wherein said oxidation and cleavage reaction is carried out with a permanganate as an oxidant and under an acidic condition.

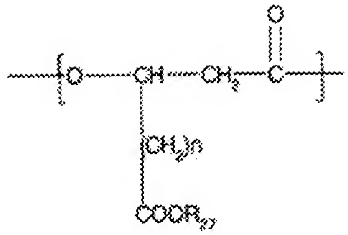
[Claim 24] The producing method according to any one of claims 17 to 21, wherein said oxidation and cleavage reaction is carried out with ozone.

[Claim 25] A method for producing a polyhydroxy alkanoate copolymer, characterized in employing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule as a starting material,

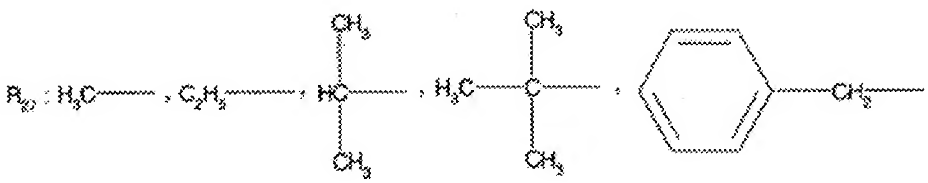
and executing a hydrolysis in the presence of an acid or an alkali or executing a hydrogenolysis including a catalytic reduction,

thereby generating a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[Chemical Formula 90]

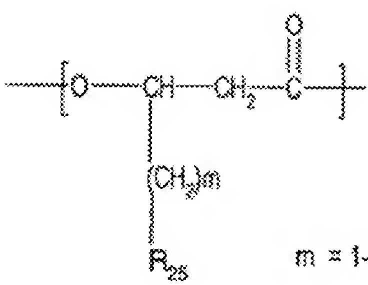


$n = 1\text{-}8$ (32)



in which n represents an integer selected within a range indicated in the chemical formula; R_{27} represents any of residues indicated in the chemical formula; and in case plural units are present, n and R_{27} may be the same or different for each unit;

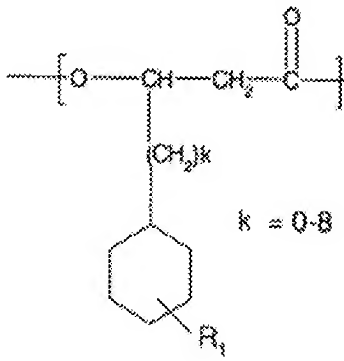
[Chemical Formula 91]



$m = 1\text{-}8$ (27)

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} includes a residue having any of a phenyl structure and a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit;

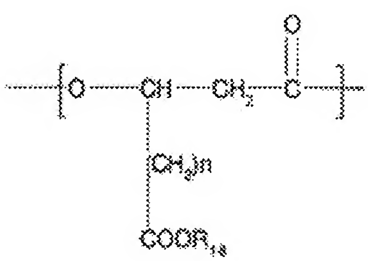
[Chemical Formula 92]



(3)

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit; and

[Chemical Formula 93]

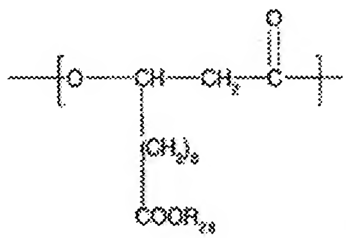


n = 1-8 (19)

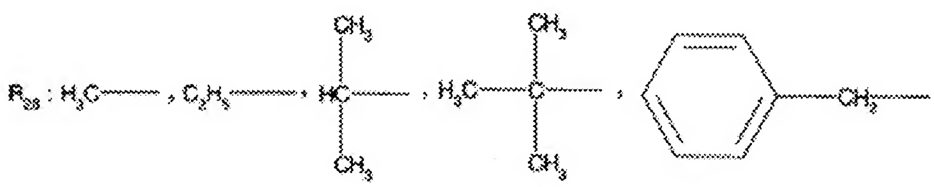
in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

[Claim 26] The polyhydroxy alkanoate copolymer according to claim 25, wherein the 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) is any one of a 3-hydroxy-11-alkoxycarbonylundecanoic acid unit represented by a chemical formula (33):

[Chemical Formula 94]

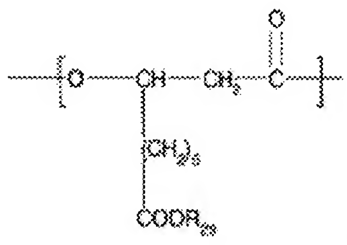


(33)

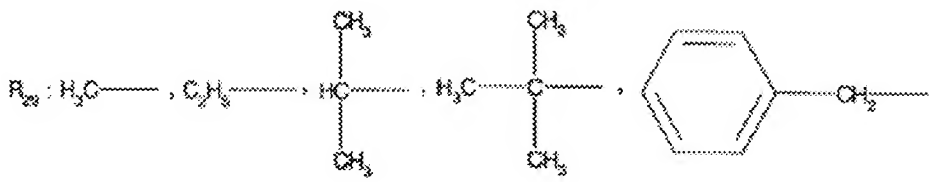


(R_{28} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{28} may be the same or different for each unit), a 3-hydroxy-9-alkoxycarboxynonanoic acid unit represented by a chemical formula (34):

[Chemical Formula 95]



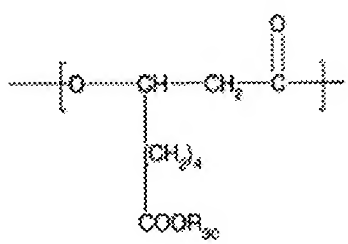
(34)



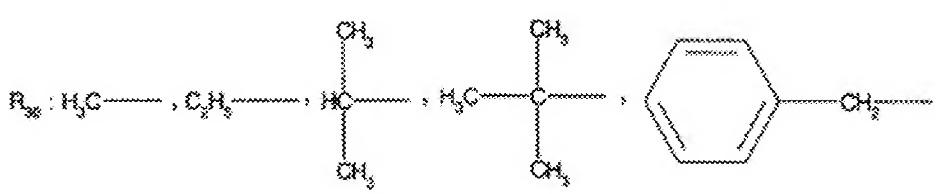
(R_{29} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{29} may be the same or different for each unit),

a 3-hydroxy-7-alkoxycarboxyheptanoic acid unit represented by a chemical formula (35):

[Chemical Formula 96]



(35)

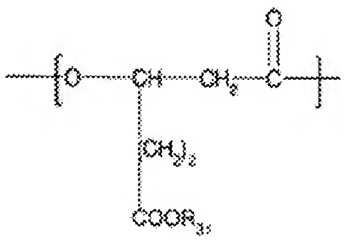


(R_{30} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{30} may be the same or different for each unit), and

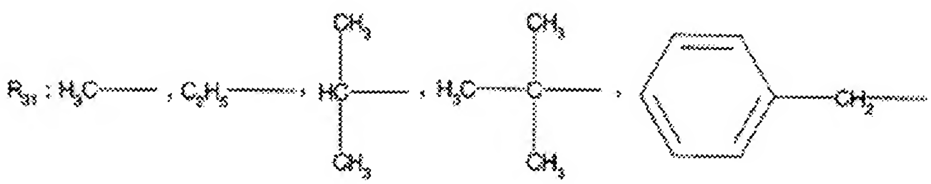
a 3-hydroxy-5-alkoxycarboxyvaleric acid unit

represented by a chemical formula (36):

[Chemical Formula 97]



(36)

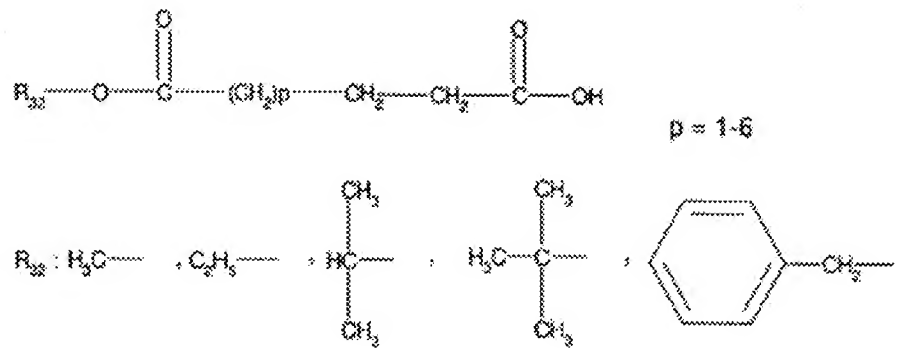


(R_{31} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{31} may be the same or different for each unit).

[Claim 27] The method for producing a polyhydroxy alkanoate copolymer including the 3-hydroxy-ω-carboxyalkanoic acid according to claim 25 or 26 hydro-synthesized by a microorganism having an ability of producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

from a dicarboxylic acid monoester compound represented by a chemical formula (37):

[Chemical Formula 98]

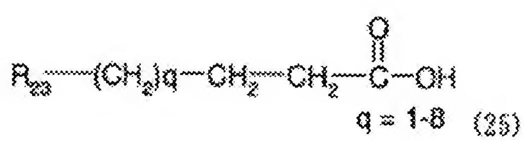


(37)

in which p represents an integer selected within a range indicated in the chemical formula; and R_{32} represents any of residues indicated in the chemical formula;

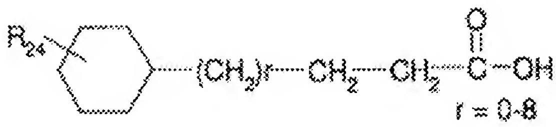
and at least a compound represented by a chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by a chemical formula (26) as starting materials:

[Chemical Formula 99]



in which q represents an integer selected within a range indicated in the chemical formula; and R_{23} includes a residue having a phenyl structure or a thienyl structure;

[Chemical Formula 100]

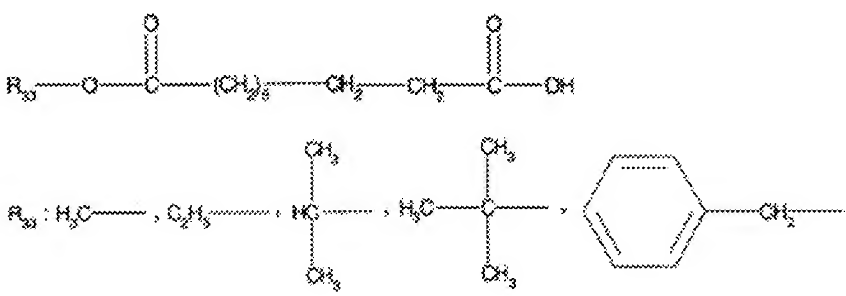


(26)

in which R_{24} represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula.

[Claim 28] The polyhydroxy alkanoate copolymer according to claim 27, wherein the dicarboxylic acid monoester compound represented by the chemical formula (37) is any one of a sebacic acid monoester compound represented by a chemical formula (38):

[Chemical Formula 101]

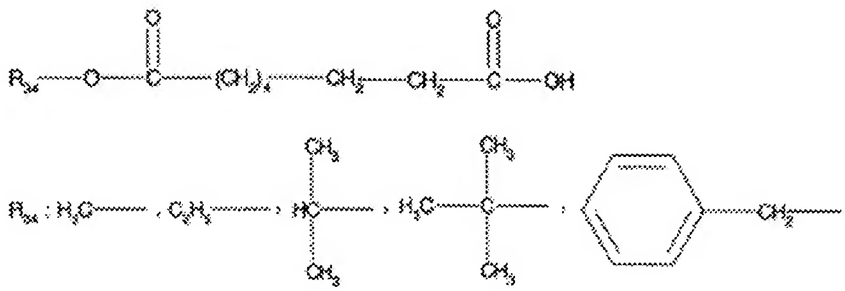


(38)

(R_{33} represents any of residues indicated in the chemical formula), or

a suberic acid monoester compound represented by a chemical formula (39):

[Chemical Formula 102]

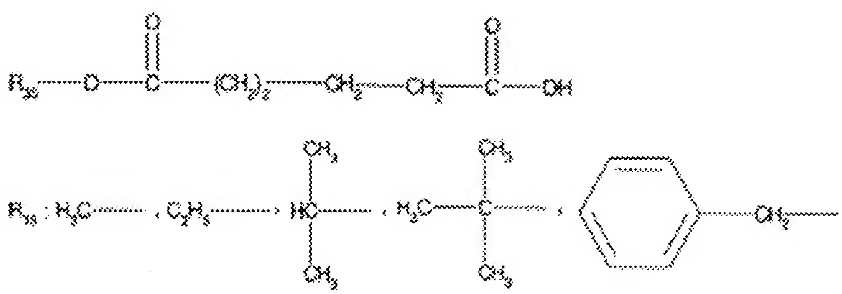


(39)

(R_{34} represents any of residues indicated in the chemical formula), or

a adipic acid monoester compound represented by a chemical formula (40):

[Chemical Formula 103]



(40)

(R_{35} represents any of residues indicated in the chemical formula).

[Claim 29] The method for producing a polyhydroxy alkanoate copolymer including at least the 3-hydroxy-ω-carboxyalkanoic acid according to claim 27 or 28 in a molecule, which hydro-synthesizes a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) by cultivating a microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by a chemical formula

(37), and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by a chemical formula (26).

[Claim 30] The method for producing a polyhydroxy alkanoate copolymer according to claim 29, wherein said microorganism is cultured in a culture medium including, in addition to at least a dicarboxylic acid monoester compound represented by the chemical formula (37), and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar, a linear alkanoic acid with 4 to 12 carbon atoms or a salt thereof.

[Claim 31] The method for producing a polyhydroxy alkanoate copolymer according to claim 30, wherein for culturing said organism, the peptide to be added to the culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of piruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; amino acid or salt thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid,

aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[Claim 32] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 27 to 31, characterized in including a step of culturing said microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by the chemical formula (37) and at least a compound represented by the chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by the chemical formula (26), and recovering a polyhydroxy alkanoate copolymer including simultaneously at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) and a 3-hydroxy-ω-alkanoic acid unit represented by the chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by said microorganism, from cells of the microorganism.

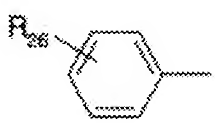
[Claim 33] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 27 to 32, wherein said microorganism is a microorganism belonging to Pseudomonas genus.

[Claim 34] The method for producing a polyhydroxy alkanoate copolymer according to claim 33, wherein said microorganism is at least one of Pseudomonas cichorii YN2 strain (FERM BP-7375), Pseudomonas cichorii H45 strain (FERM BP-7374), Pseudomonas jessenii P161 (FERM BP-7376) and Pseudomonas putida P91 (FERM BP-7373).

[Claim 35] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 25 to 34, wherein R_{25} in the chemical formula (27) and R_{23} in the chemical formula (25), each representing a residue having a phenyl structure or a thienyl structure, represents at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (31):

[Chemical Formula 104]

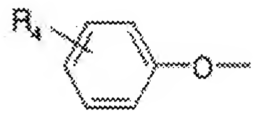


(31)

represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[Chemical Formula 105]

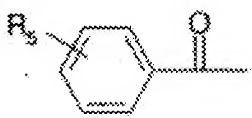


(9)

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 106]

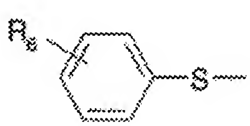


(10)

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 107]

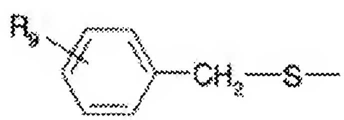


(11)

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 108]

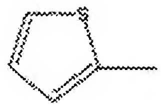


(12)

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[Chemical Formula 109]

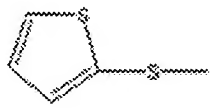


(13)

represents a 2-thienyl group;

the chemical formula (14):

[Chemical Formula 110]

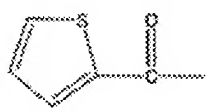


(14)

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[Chemical Formula 111]

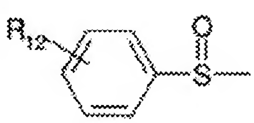


(15)

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 112]



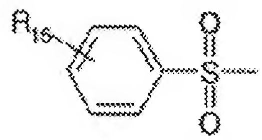
(16)

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a

$(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 113]

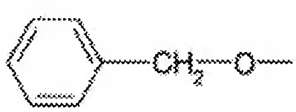


(17)

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 114]



(18)

represents a (phenylmethyl)oxy group.

[Detailed Description of the Invention]

[0001]

[Field of the invention]

The present invention relates to a polyhydroxy

alkanoate (hereinafter also abbreviated as PHA) copolymer including a novel unit having a double bond and a producing method therefor utilizing microorganisms, also polyhydroxy alkanoate copolymer including a novel unit having a carboxyl group or a salt thereof, derived from the aforementioned copolymer, and a producing method therefor.

[0002]

[Background Art]

It has already been reported that various microorganisms produce poly-3-hydroxybutyric acid (PHB) or other poly-3-hydroxyalkanoate (PHA) and accumulate such products therein ("Biodegradable Plastic Handbook", edited by Biodegradable Plastics Society, NTS Inc. pp. 178-197 (1995) (Non-patent Document 1)). Such PHA produced by the microorganisms can be utilized for producing various products. Also the PHA produced by microorganisms, being biodegradable, has the advantage that it can be completely decomposed by the microorganisms. Therefore the PHA produced by microorganisms, when discarded, unlike the various conventional synthesized polymers, would not cause pollution resulting from remaining in the natural environment. Also the PHA produced by microorganisms shows satisfactory affinity to the living tissues and is expected in the applications as the soft material for medical use.

[0003]

It is known that such microorganism-produced PHA can have various compositions and structures depending on the type, medium composition, culturing conditions or the like of microorganisms used for the production. So far studies related to the control of these compositions and structures were mainly conducted from the viewpoint of improving physical properties of PHA.

[0004]

[1] First of all, as biosynthesis of PHA, in which monomer units with relatively simple structures are polymerized, including 3-hydroxybutyric acid (hereinafter abbreviated as "3HB"), the following can be pointed out.

[0005]

(a) Biosynthesis containing 3HB and 3-hydroxyvaleric acid (hereinafter referred to as "3HV")

Japanese Patent Publication Nos. H6-15604, H7-14352, H8-19227, etc.: Japanese Patent Application Laid-Open No. H5-7492 (Patent Documents 1 to 4)

(b) Biosynthesis containing 3HB and 3-hydroxyhexanoic acid (hereinafter referred to as "3HHx")

Japanese Patent Application Laid-Open Nos. H5-93049 and H7-265065 (Patent Documents 5 and 6)

(c) Biosynthesis containing 3HB and 4-hydroxybutyric acid (hereinafter referred to as "4HB")

Japanese Patent Application Laid-Open No. H9-191893 (Patent Document 7)

(d) Biosynthesis containing 3-hydroxyalkanoate with 6 to 12 carbon atoms

Japanese Patent No. 2642937 (Patent Document 8)

(e) Biosynthesis using a single fatty acid as a carbon source; the product is almost identical with the one by (d).

Appl. Environ. Microbiol., 58 (2), 746 (1992) (Non-patent Document 2)

Every one of these is PHA comprised of a monomer unit having an alkyl group in a side chain synthesized by β-oxidation of a hydrocarbon or the like or fatty acid synthesis from a sugar with the help of microorganisms, namely "unusual PHA."

[0006]

[2] However, for wider application of microorganism-produced PHA, for example for application as functional polymer, PHA having a substituent other than alkyl group in the side chain, namely "unusual PHA," is anticipated to be extremely useful. Examples of hopeful substituents for this purpose include a group containing an aromatic ring (phenyl group, phenoxy group etc.), an unsaturated hydrocarbon group, an ester group, an allyl group, a cyano group, a halogenated hydrocarbon group and an epoxide present on the side chain. Among these, PHA having an aromatic

ring is actively investigated as follows:

[0007]

(a) PHA containing a phenyl group or a partially substituted group thereof:

Makromol. Chem. 191, 1957-1965 (1990) (Non-patent Document 3) and Macromolecules, 24, 5256-5260 (1991) (Non-patent Document 4) report that Pseudomonas oleovorans produces PHA containing 3-hydroxy-5-phenylvaleric acid as a unit, from 5-phenylvaleric acid as a substrate.

[0008]

Macromolecules, 29, 1762-1766 (1996) (Non-patent Document 5) reports that Pseudomonas oleovorans produces PHA containing 3-hydroxy-5-(p-tolyl)valeric acid as a unit, from 5-(p-tolyl)valeric acid as a substrate.

[0009]

Macromolecules, 32, 2889-2895 (1999) (Non-patent Document 6) reports that Pseudomonas oleovorans produces PHA containing 3-hydroxy-5-(2,4-dinitrophenyl)valeric acid and 3-hydroxy-5-(p-nitrophenyl)valeric acid as units, from 5-(2,4-dinitrophenyl)valeric acid as a substrate.

[0010]

(b) PHA containing phenoxy group or a partially substituted group thereof:

Macromol. Chem. Phys., 195, 1665-1672 (1994) (Non-

patent Document 7) reports that Pseudomonas oleovorans produces a PHA copolymer containing 3-hydroxy-5-hydroxyvaleric acid and 3-hydroxy-9-phenoxynonanoic acid as the units, from 11-phenoxyundecanoic acid as a substrate.

[0011]

Also Japanese Patent No. 2989175 (Patent Document 8) discloses inventions relating to a homopolymer constituted of a 3-hydroxy-5-(monofluorophenoxy) pentanoate (3H5(MFP)P) unit or a 3-hydroxy-5-(difluorophenoxy) pentanoate (3H5(DFP)P) unit, a copolymer containing either a 3H5(MFP)P unit or a 3H5(DFP)P unit or both, a novel strain of Pseudomonas putida capable of producing these polymers, and a method for producing the aforementioned polymers utilizing bacteria of genus Pseudomonas. This patent specification teaches, as the effects of such inventions, that PHA polymer having a phenoxy group substituted with 1 or 2 fluorine atoms at the end of the side chain can be biosynthesized from a long-chain fatty acid having a fluorine substituent and that thus produced PHA has a high melting point and is capable of providing stereoregularity and water repellency while maintaining satisfactory working properties.

[0012]

In addition to the fluorine-substituted PHA having a fluorine substitution on the aromatic ring in the

unit, there are also investigated PHA having a cyano group or a nitro group on the aromatic ring in the unit.

[0013]

Can. J. Microbiol., 41, 32-43 (1995) (Non-patent Document 8) and Polymer International, 39, 205-213 (1996) (Non-patent Document 9) report production of PHA, containing 3-hydroxy-6-(p-cyanophenoxy) hexanoic acid or 3-hydroxy-6-(p-nitrophenoxy) hexanoic acid as the monomer unit, by Pseudomonas oleovorans ATCC 29347 strain and Pseudomonas putida KT2442 strain, from octanoic acid and 6-(p-cyanophenoxy) hexanoic acid or 6-(p-nitrophenoxy) hexanoic acid as a substrate.

[0014]

These references relate to PHA having an aromatic ring on the side chain, instead of alkyl groups of the usual PHA, which are effective in obtaining polymer with physical properties resulting from such aromatic ring.

[0015]

[3] Also as a new category not limited to changes in the physical properties, investigations are also made for producing PHA having an appropriate functional group on the side chain, thereby obtaining PHA with new functions utilizing such substituent.

[0016]

As a specific method for such purpose, investigations are also made for producing PHA having,

in a unit thereof, reactive group such as a bromo group or a vinyl group with a high activity for example in an addition reaction to introduce an arbitrary function group in a side chain of the polymer by a chemical conversion utilizing such active group, in order to obtain PHA of multiple functions.

[0017]

Macromol. Rapid Commun., 20, 91-94 (1999) (Non-patent Document 10) reports production of PHA having a bromo group in a side chain by Pseudomonas oleovorans, and modifying the side chain with a thiolated product of acetylated maltose thereby synthesizing PHA different in solubility and hydrophilicity.

[0018]

Polymer, 41, 1703-1709 (2000) (Non-patent Document 11) reports producing PHA, having 3-hydroxyalkenic acid with an unsaturated bond (vinyl group) at an end of a side chain as a monomer unit, by Pseudomonas oleovorans with 10-undecenoic acid as a substrate, followed by an oxidation reaction with potassium permanganate to synthesize 3-hydroxyalkanoic acid having a diol at the end of the side chain, which PHA is reported to show such a change in solubility in solvents, as becoming soluble in polar solvents such as methanol, an acetone-water (80/20, v/v) or dimethylsulfoxide and insoluble in non-polar solvents such as chloroform, tetrahydrofuran or acetone.

[0019]

Also Macromolecules, 31, 1480-1486 (1996) (Non-patent Document 12) reports production of a polyester, including a unit having vinyl group in a side chain by Pseudomonas oleovorans and epoxylating the vinyl group to obtain a polyester having an epoxy group in the side chain.

[0020]

Also Polymer, 35, 2090-2097 (1994) (Non-patent Document 13) reports a crosslinking reaction within the polyester molecule utilizing the vinyl group in the side chain of polyester, thereby improving physical properties of polyester.

[0021]

Macromolecular chemistry, 4, 289-293 (2001) (Non-patent Document 14) reports producing PHA, including 3-hydroxy-10-undecenoic acid as a monomer unit, from 10-undecenoic acid as a subsrate, and then executing an oxidation reaction with potassium permanganate to obtain PHA including 3-hydroxy-10-carboxydecanoic acid as a monomer unit, and reports an improvement in a decomposition thereof.

[0022]

Furthermore, in order to modify physical properties of PHA having an active group in a unit and to actually utilize it as a polymer, it has been studied biosynthesis of a PHA copolymer including a

unit having the active group and other units; Macromolecules, 25, 1852-1857 (1992) (Non-patent Document 15) reports production of a PHA copolymer including a 3-hydroxy-ω-bromoalkanoic acid unit and a linear alkanoic acid unit by Pseudomonas oleovorans in the presence of an ω-bromoalkanoic acid such as 11-bromoundecanoic acid, 8-bromooctanoic acid or 6-bromohexanoic acid and n-nonanoic acid.

[0023]

Such PHA having a highly reactive active group such as a bromo group or a vinyl group can be subjected to introduction of various functional groups or chemical modification, and such a group can be a crosslinking point for a polymer, so that it is very useful means for realizing multiple functions in PHA.

[0024]

Also technologies related to the present invention include a technology of oxidizing and cleaving a carbon-carbon double bond with an oxidant to obtain a carboxylic acid (Patent Document 9 and Non-patent Documents 16 to 19)

[0025]

[Patent Document 1]

Japanese Patent Publication No. H6-15604

[Patent Document 2]

Japanese Patent Publication No. H7-14352

[Patent Document 3]

Japanese Patent Publication No. H8-19227

[Patent Document 4]

Japanese Patent Application Laid-Open No. H5-7492

[Patent Document 5]

Japanese Patent Application Laid-Open No. H5-93049

[Patent Document 6]

Japanese Patent Application Laid-Open No. H7-265065

[Patent Document 7]

Japanese Patent Application Laid-Open No. H9-191893

[Patent Document 8] Japanese Patent No. 2989175

[Patent Document 9]

Japanese Patent Application Laid-Open No. S59-190945

[0026]

[Non-patent Document 1]

“Biodegradable Plastic Handbook", edited by Biodegradable Plastics Society, NTS Inc. pp. 178-197 (1995)

[Non-patent Document 2]

Appl. Environ. Microbiol., 58 (2), 746 (1992)

[Non-patent Document 3]

Makromol. Chem. 191, 1957-1965 (1990)

[Non-patent Document 4]

Macromolecules, 24, 5256-5260 (1991)

[Non-patent Document 5]

Macromolecules, 29, 1762-1766 (1996)

[Non-patent Document 6]

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[Non-patent Document 13]

Polymer, 35, 2090-2097 (1994)

[Non-patent Document 14] Macromolecular chemistry, 4, 289-293 (2001)

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[Non-patent Document 17]

Org. Synth., 4, 698 (1963)

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[Non-patent Document 19]

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[0027]

[Problem to be Solved by the Invention]

However, the copolymers in the foregoing reports are comprised of a monomer unit having a carboxyl group at the end of a side chain and a monomer unit having a linear alkyl group (usual PHA). Because of this, this polymer has problems, such as a low glass transition temperature. On the other hand, there is no report on copolymers including unusual PHA having on the side chain thereof a substituent other than a linear alkyl group, such as a phenyl structure, a thienyl structure or a cyclohexyl structure. Thus such polyhydroxy alkanoate and a producing method therefor have been required.

[0028]

Also PHA having a vinyl group as an active group is a PHA copolymer with a monomer unit having a linear alkyl group(usual PHA), its low glass transition temperature and low melting point are undesirable properties in the working and the use of the polymer.

[0029]

Because of the above-described situation, there have been a demand for PHA having an active group and a production method therefor, such that PHA can be produced by a microorganism at a high yield, the unit

ratio of the active group can be controlled, and its physical properties can be freely regulated not to limit its application as a polymer.

[0030]

[Means for Solving the Problem]

As a result of intensive investigations, the present inventors have found a method of synthesizing a PHA formed by copolymerization of a unit having a vinyl group or a carboxyl group of a high reactivity, and a unit having either one of a phenyl structure, a thienyl structure and a cyclohexyl structure which can contribute to an improvement of physical properties of the polymer, and have thus made the present invention.

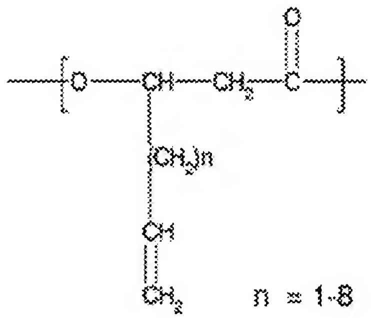
The present invention is outlined in the following.

[0031]

[1] A polyhydroxy alkanoate copolymer characterized in including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[0032]

[Chemical Formula 115]



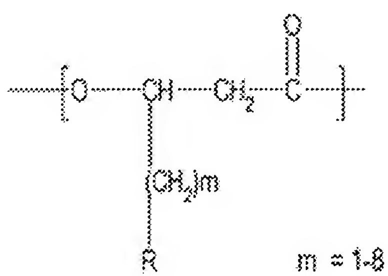
(1)

[0033]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0034]

[Chemical Formula 116]



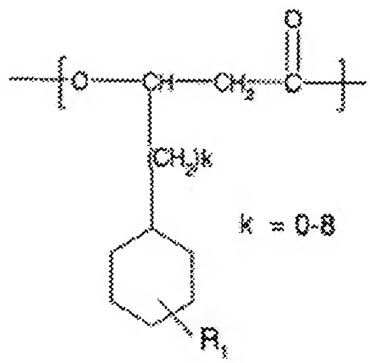
(2)

[0035]

in which m represents an integer selected within a range indicated in the chemical formula; R represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit;

[0036]

[Chemical Formula 117]



(3)

[0037]

in which R_1 being a substituent on a cyclohexyl group represents a hydrogen atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit.

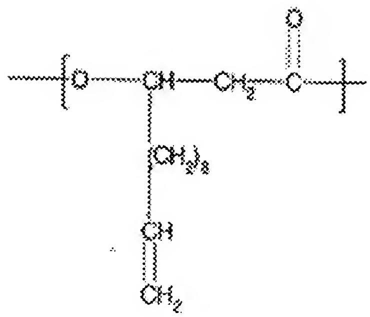
[2] The polyhydroxy alkanoate copolymer according to [1], wherein the 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) is any one of

[0038]

a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

[0039]

[Chemical Formula 118]



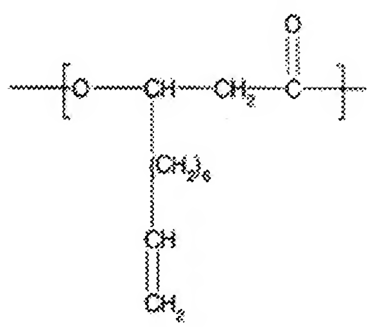
(4)

[0040]

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

[0041]

[Chemical Formula 119]



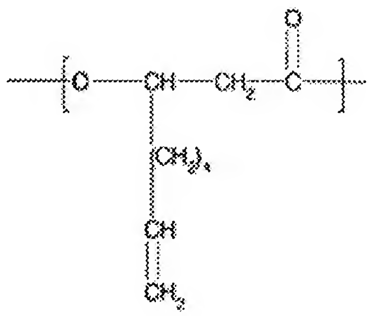
(5)

[0042]

a 3-hydroxy-8-nonenoic acid unit represented by a chemical formula (6): and

[0043]

[Chemical Formula 120]



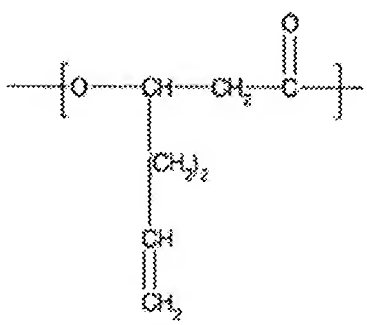
(6)

[0044]

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7):

[0045]

[Chemical Formula 121]



(7).

[0046]

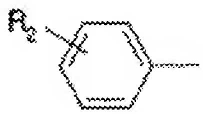
[3] The polyhydroxy alkanoate copolymer according to [1] or [2], wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from the group consisting of chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0047]

the chemical formula (8):

[0048]

[Chemical Formula 122]



(8)

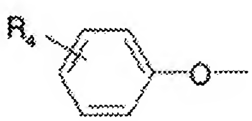
[0049]

represents a group of non-substituted or substituted phenyl groups in which R_2, a substituent on an aromatic ring and represents an H atom, represents a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a $COOR_3$ group (R_3 represents an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[0050]

[Chemical Formula 123]



(9)

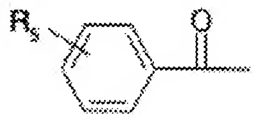
[0051]

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0052]

[Chemical Formula 124]



(10)

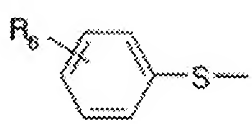
[0053]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11)

[0054]

[Chemical Formula 125]



(11)

[0055]

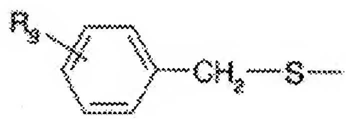
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa,

OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0056]

[Chemical Formula 126]



(12)

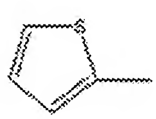
[0057]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0058]

[Chemical Formula 127]



(13)

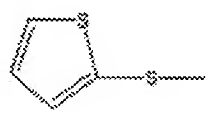
[0059]

represents a 2-thienyl group;

the chemical formula (14)

[0060]

[Chemical Formula 128]



(14)

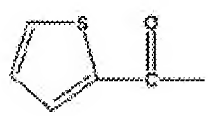
[0061]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0062]

[Chemical Formula 129]



(15)

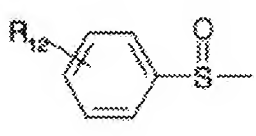
[0063]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0064]

[Chemical Formula 130]



(16)

[0065]

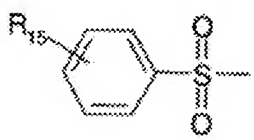
represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0066]

[Chemical Formula 131]



(17)

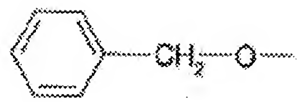
[0067]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[0068]

[Chemical Formula 132]



(18)

[0069]

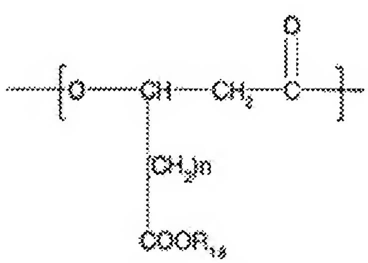
represents a (phenylmethyl)oxy group.

[0070]

[4] A polyhydroxy alkanoate copolymer characterized in including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

[0071]

[Chemical Formula 133]



$n = 1\text{-}8$ (19)

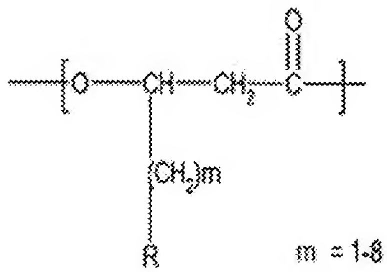
[0072]

in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom or a K atom: and in case plural units are present, n and R_{18} may be the same or

different for each unit;

[0073]

[Chemical Formula 134]



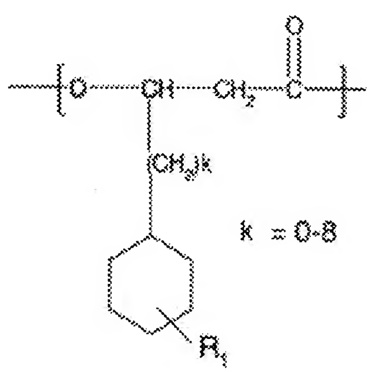
(2)

[0074]

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit; and

[0075]

[Chemical Formula 135]



(3)

[0076]

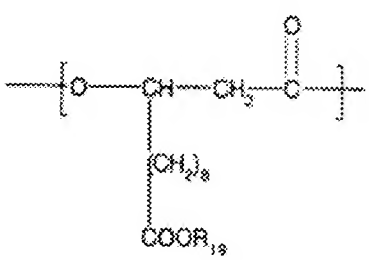
in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group,

a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit.

[5] The polyhydroxy alkanoate copolymer according to [4], wherein the 3-hydroxy-ω-carboxyalkanoic acid unit represented by the chemical formula (19) is any one of a 3-hydroxy-11-carbonylundecanoic acid unit represented by a chemical formula (20):

[0077]

[Chemical Formula 136]



(20)

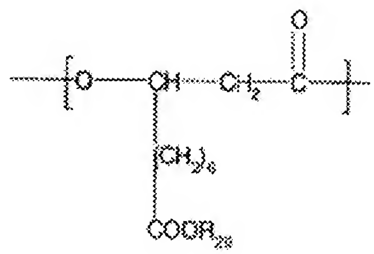
[0078]

(R_{19} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{19} may be the same or different for each unit),

a 3-hydroxy-9-carboxynonanoic acid unit represented by a chemical formula (21):

[0079]

[Chemical Formula 137]



(21)

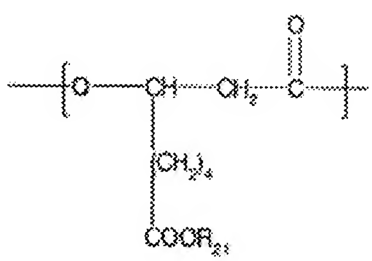
[0080]

(R_{20} represents an H atom, a Na atom or a K atom and in case plural units are present; and R_{20} may be the same or different for each unit),

a 3-hydroxy-7-carboxyheptanoic acid unit represented by a chemical formula (22):

[0081]

[Chemical Formula 138]



(22)

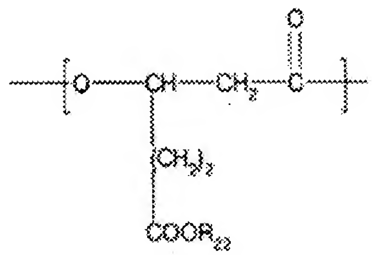
[0082]

(R_{21} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{21} may be the same or different for each unit), and

a 3-hydroxy-5-carboxyvaleric acid unit represented by a chemical formula (23):

[0083]

[Chemical Formula 139]



(23)

[0084]

(R_{22} represents an H atom, a Na atom or a K atom; and in case plural units are present, R_{22} may be the same or different for each unit).

[0085]

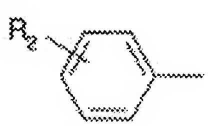
[6] The polyhydroxy alkanoate copolymer according to [4] or [5], wherein R in the chemical formula (2), represents a residue having a phenyl structure or a thienyl structure selected from chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17), and (18):

[0086]

the chemical formula (8):

[0087]

[Chemical Formula 140]



(8)

[0088]

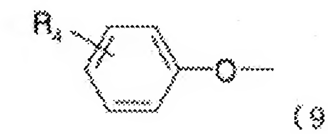
represents a group of non-substituted or substituted phenyl groups in which R_2 represents a substituent on an aromatic ring and represents an H atom, a halogen

atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH{=}CH_2$ group, a $COOR_3$ group (R_3 representing an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[0089]

[Chemical Formula 141]



(9)

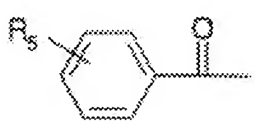
[0090]

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0091]

[Chemical Formula 142]



(10)

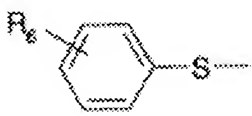
[0092]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0093]

[Chemical Formula 143]



(11)

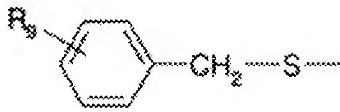
[0094]

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0095]

[Chemical Formula 144]



(12)

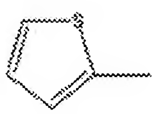
[0096]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0097]

[Chemical Formula 145]



(13)

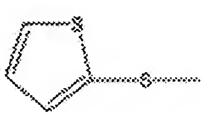
[0098]

represents a 2-thienyl group;

the chemical formula (14):

[0099]

[Chemical Formula 146]



(14)

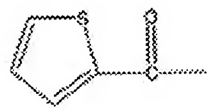
[0100]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0101]

[Chemical Formula 147]



(15)

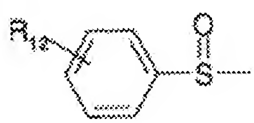
[0102]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0103]

[Chemical Formula 148]



(16)

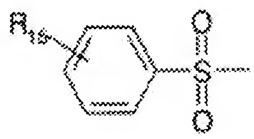
[0104]

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0105]

[Chemical Formula 149]



(17)

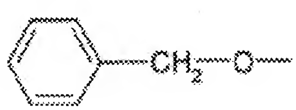
[0106]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[0107]

[Chemical Formula 150]



(18)

[0108]

represents a (phenylmethyl)oxy group.

[0109]

[7] The polyhydroxy alkanoate copolymer according to any one of [1] to [6], wherein a number-averaged

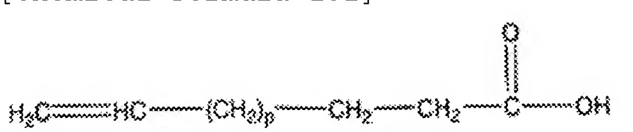
molecular weight is within a range from 1000 to 1000000.

[0110]

[8] A method for producing a polyhydroxy alkanoate copolymer characterized in including a biosynthesis by a microorganism having an ability of producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, from at least an ω-alkenoic acid represented by a chemical formula (24) and at least a compound represented by a chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by a chemical formula (26) as starting materials:

[0111]

[Chemical Formula 151]



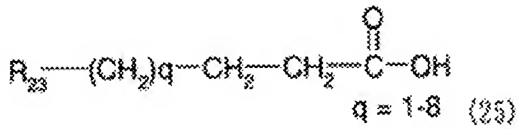
p = 1-8 (24)

[0112]

in which p represents an integer selected within a range indicated in the chemical formula;

[0113]

[Chemical Formula 152]

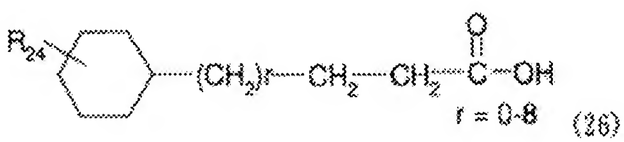


[0114]

in which q represents an integer selected within a range indicated in the chemical formula; and R_{23} includes a residue having a phenyl structure or a thienyl structure;

[0115]

[Chemical Formula 153]

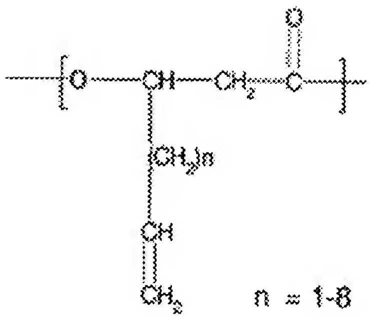


[0116]

in which R_{24} represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula;

[0117]

[Chemical Formula 154]



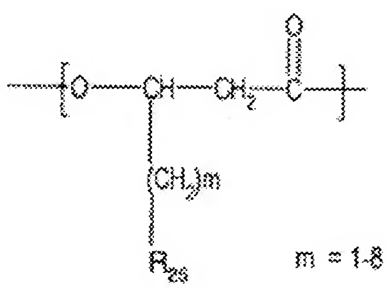
(1)

[0118]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0119]

[Chemical Formula 155]



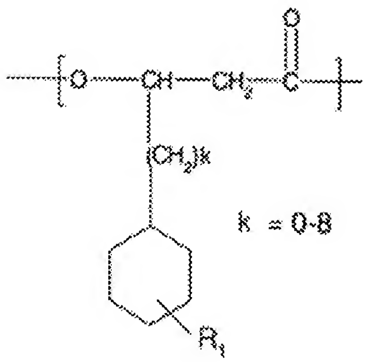
(27)

[0120]

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit; and

[0121]

[Chemical Formula 156]



(3)

[0122]

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

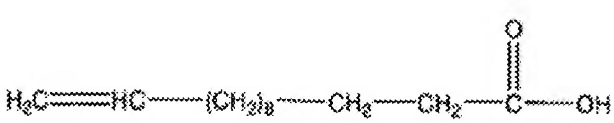
[9] The method for producing a polyhydroxy alkanoate copolymer according to [8], wherein the ω-alkenoic acid represented by the chemical formula (24) is

[0123]

a 12-tridecenoic acid represented by a chemical formula (28): or

[0124]

[Chemical Formula 157]



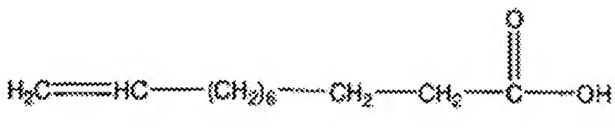
(28)

[0125]

a 10-undecenoic acid represented by a chemical formula (29): or

[0126]

[Chemical Formula 158]



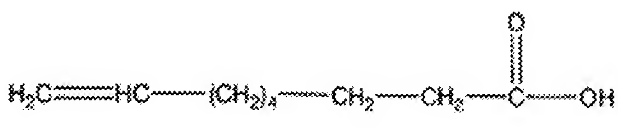
(29)

[0127]

a 8-nonenoic acid unit represented by a chemical formula (30):

[0128]

[Chemical Formula 159]



(30)

.

[0129]

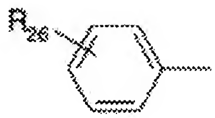
[10] The method for producing a polyhydroxy alkanoate copolymer according to [8] or [9], wherein R_{23} in the chemical formula (25) and R_{25} in the chemical formula (27), each represents a residue having a phenyl structure or a thienyl structure, are selected from chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0130]

the chemical formula (31):

[0131]

[Chemical formula 160]



(31)

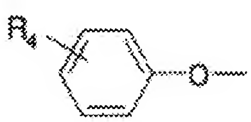
[0132]

represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[0133]

[Chemical Formula 161]



(9)

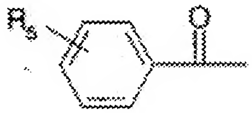
[0134]

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0135]

[Chemical Formula 162]



(10)

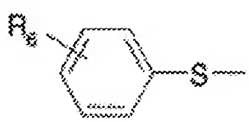
[0136]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0137]

[Chemical Formula 163]



(11)

[0138]

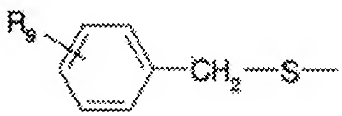
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a

$(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0139]

[Chemical Formula 164]



(12)

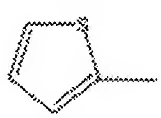
[0140]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0141]

[Chemical Formula 165]



(13)

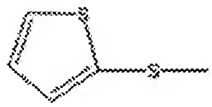
[0142]

represents a 2-thienyl group;

the chemical formula (14):

[0143]

[Chemical Formula 166]



(14)

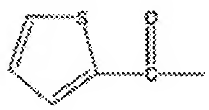
[0144]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0145]

[Chemical Formula 167]



(15)

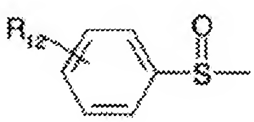
[0146]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0147]

[Chemical Formula 168]



(16)

[0148]

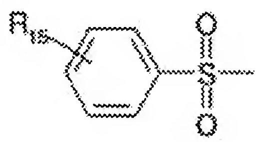
represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H,

Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a (CH3)$_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0149]

[Chemical Formula 169]



(17)

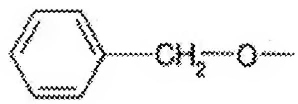
[0150]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[0151]

[Chemical Formula 170]



(18)

[0152]

represents a (phenylmethyl)oxy group.

[0153]

[11] The method for producing a polyhydroxy alkanoate copolymer according to any one of [8] to [10], wherein the microorganism is cultured in a culture medium including at least a ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26).

[0154]

[12] The method for producing a polyhydroxy alkanoate copolymer according to [11], wherein the microorganism is cultured in a culture medium including, in addition to at least an ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar, a linear alkanoic acid with 4 to 12 carbon atoms or a salt thereof.

[0155]

[13] The method for producing a polyhydroxy

alkanoate copolymer according to [12] wherein for culturing the organism, the peptide to be added to the culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of piruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; amino acid or salt thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid, aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[0156]

[14] The method for producing a polyhydroxy alkanoate copolymer according to any one of [8] to [13], characterized in including a step of culturing the microorganism in a culture medium including at least an ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by the chemical formula (26), and recovering a polyhydroxy alkanoate copolymer including simultaneously at least a 3-

hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) and a 3-hydroxy-ω-alkanoic acid unit represented by the chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by the microorganism, from cells of the microorganism.

[0157]

[15] The method for producing a polyhydroxy alkanoate copolymer according to any one of [8] to [14], wherein the microorganism is a microorganism belonging to Pseudomonas genus.

[0158]

[16] The method for producing a polyhydroxy alkanoate copolymer according to [15], wherein the microorganism is at least one of Pseudomonas cichorii YN2 strain (FERM BP-7375), Pseudomonas cichorii H45 strain (FERM BP-7374), Pseudomonas jessenii P161 (FERM BP-7376) and `Pseudomonas putida P91 (FERM BP-7373).

[0159]

[17] A method for producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule comprising the steps of:

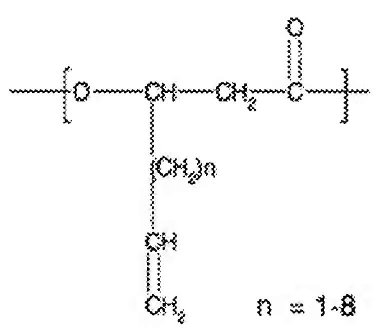
preparing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule as a starting material, and

oxidizing and cleaving a double bond portion in the polyhydroxy alkanoate represented in the chemical formula (1) thereby

generating a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[0160]

[Chemical Formula 171]



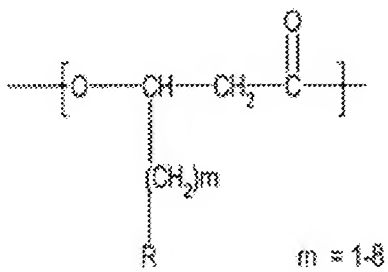
(1)

[0161]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0162]

[Chemical Formula 172]



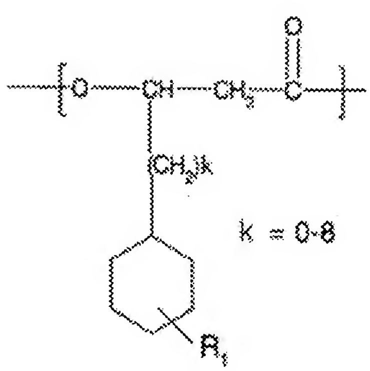
(2)

[0163]

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure and a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit;

[0164]

[Chemical Formula 173]



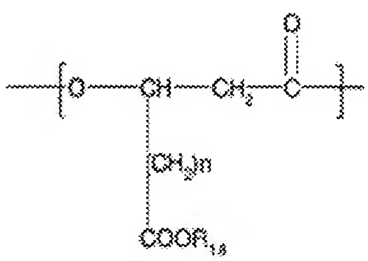
(3)

[0165]

in which R_1 represents a substituent on a cyclohexyl group selected from an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, and a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit; and

[0166]

[Chemical Formula 174]



n = 1-8 (19)

[0167]

in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

[18] The method for producing a polyhydroxy alkanoate copolymer according to [17], wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from

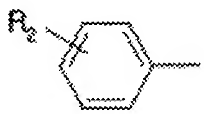
chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0168]

the chemical formula (8):

[0169]

[Chemical Formula 175]



(8)

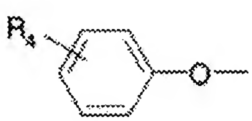
[0170]

represents a group of non-substituted or substituted phenyl groups in which R_2 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a $COOR_3$ group (R_3 representing an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

[0171]

[Chemical Formula 176]



(9)

[0172]

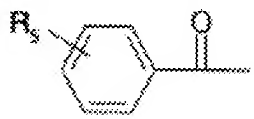
represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on

an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0173]

[Chemical Formula 177]



(10)

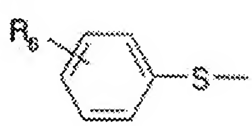
[0174]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0175]

[Chemical Formula 178]



(11)

[0176]

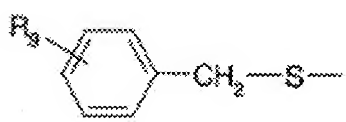
represents a group of substituted or non-substituted

phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0177]

[Chemical Formula 179]



(12)

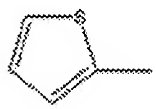
[0178]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0179]

[Chemical Formula 180]



(13)

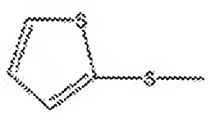
[0180]

represents a 2-thienyl group;

the chemical formula (14):

[0181]

[Chemical Formula 181]



(14)

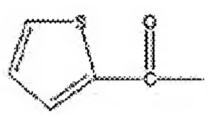
[0182]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0183]

[Chemical Formula 182]



(15)

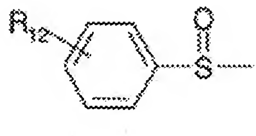
[0184]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0185]

[Chemical Formula 183]



(16)

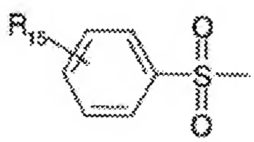
[0186]

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0187]

[Chemical Formula 184]



(17)

[0188]

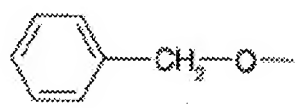
represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5; and R_{17} represents either one of OH,

ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit;

the chemical formula (18):

[0189]

[Chemical Formula 185]



(18)

[0190]

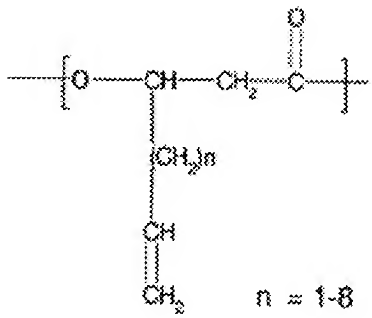
represents a (phenylmethyl)oxy group.

[0191]

[19] The method according to [17] or [18], wherein the starting material polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, is produced by a method according to any one of [8] to [16];

[0192]

[Chemical Formula 186]



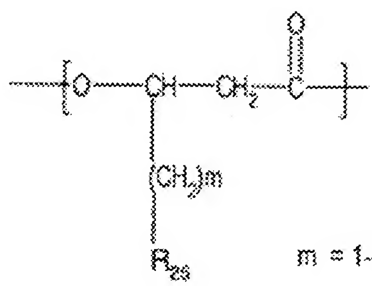
(1)

[0193]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0194]

[Chemical Formula 187]



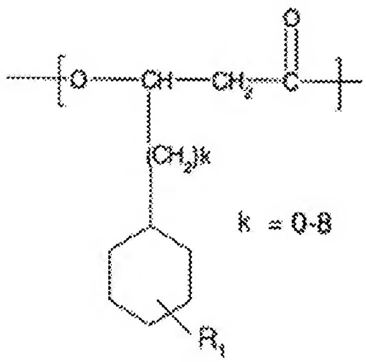
(27)

[0195]

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit; and

[0196]

[Chemical Formula 188]



(3)

[0197]

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

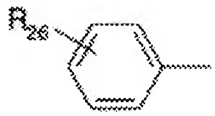
[20] The method for producing a polyhydroxy alkanoate copolymer according to [19], wherein R_{25} in the chemical formula (27), representing a residue having a phenyl structure or a thienyl structure, is at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0198]

the chemical formula (31):

[0199]

[Chemical Formula 189]


(31)

[0200]

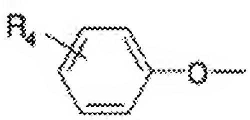
(31)

represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[0201]

[Chemical Formula 190]


(9)

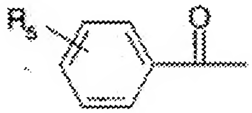
[0202]

represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0203]

[Chemical Formula 191]



(10)

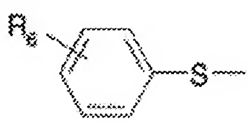
[0204]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0205]

[Chemical Formula 192]



(11)

[0206]

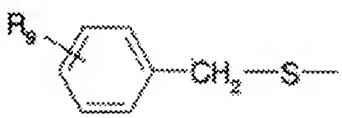
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a

$(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0207]

[Chemical Formula 193]



(12)

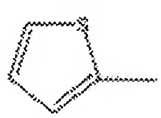
[0208]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H^7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R9 may be the same or different for each unit;

the chemical formula (13):

[0209]

[Chemical Formula 194]



(13)

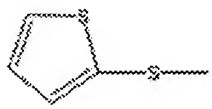
[0210]

represents a 2-thienyl group;

the chemical formula (14):

[0211]

[Chemical Formula 195]



(14)

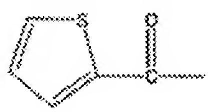
[0212]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0213]

[Chemical Formula 196]



(15)

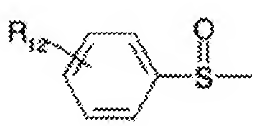
[0214]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0215]

[Chemical Formula 197]



(16)

[0216]

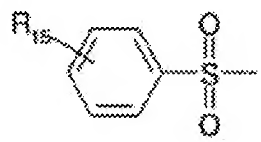
represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H,

Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0217]

[Chemical Formula 198]


(17)

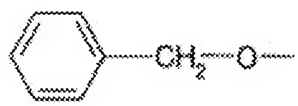
[0218]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[0219]

[Chemical Formula 199]



(18)

[0220]

represents a (phenylmethyl)oxy group.

[0221]

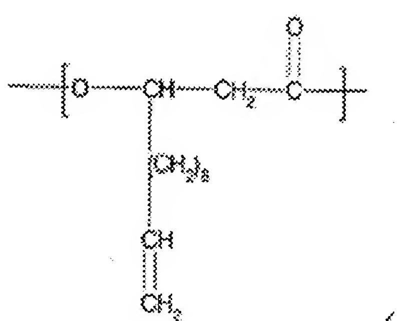
[21] The polyhydroxy alkanoate copolymer according to any one of [17] to [20], wherein the 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1) is any one of

[0222]

a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

[0223]

[Chemical Formula 200]



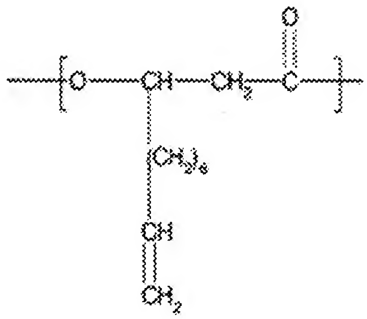
(4)

[0224]

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

[0225]

[Chemical Formula 201]



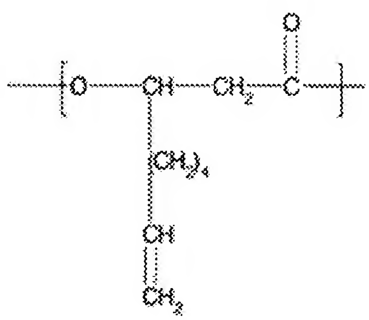
(5)

[0226]

a 3-hydroxy-8-nonenoic acid unit represented by a chemical formula (6): and

[0227]

[Chemical Formula 202]



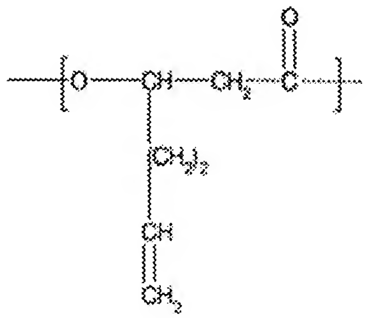
(6)

[0228]

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7)

[0229]

[Chemical Formula 203]



(7).

[0230]

[22] The producing method according to any one of [17] to [21], wherein the oxidation and cleavage reaction is carried out with an oxidant selected from a group consisting of a permanganate, a bichromate and a periodate.

[0231]

[23] The producing method according to [22], wherein the oxidation and cleavage reaction is carried out with a permanganate as an oxidant and under an acidic condition.

[0232]

[24] The producing method according to any one of [17] to [21], wherein the oxidation and cleavage reaction is carried out with ozone.

[0233]

[25] A method for producing a polyhydroxy alkanoate copolymer, characterized in employing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented

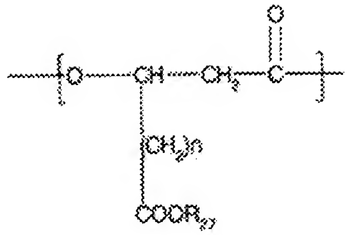
by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule as a starting material,

and executing a hydrolysis in the presence of an acid or an alkali or executing a hydrogenolysis including a catalytic reduction,

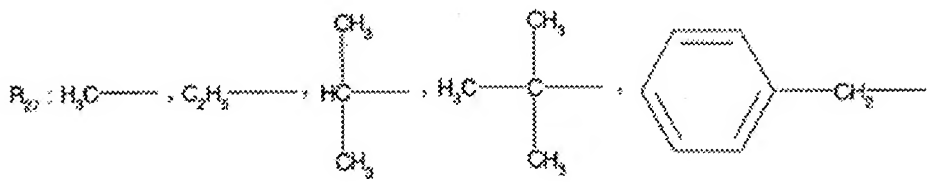
thereby generating a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[0234]

[Chemical Formula 204]



n = 1-8 (32)

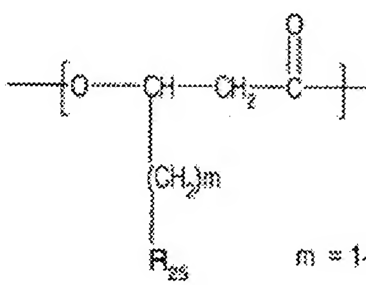


[0235]

in which n represents an integer selected within a range indicated in the chemical formula; R_{27} represents any of residues indicated in the chemical formula; and in case plural units are present, n and R_{27} may be the same or different for each unit;

[0236]

[Chemical Formula 205]



m = 1-8 (27)

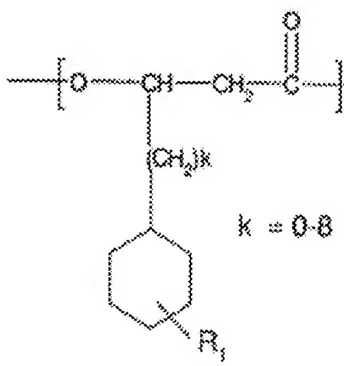
[0237]

in which m represents an integer selected within a range indicated in the chemical formula; R_{25} includes a

residue having any of a phenyl structure and a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit;

[0238]

[Chemical Formula 206]



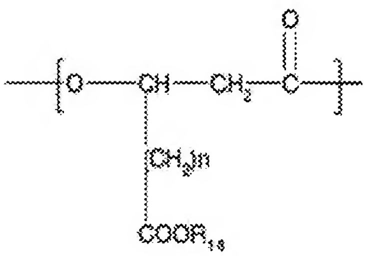
(3)

[0239]

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit; and

[0240]

[Chemical Formula 207]



n = 1-8 (19)

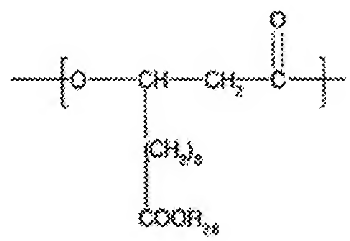
[0241]

in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

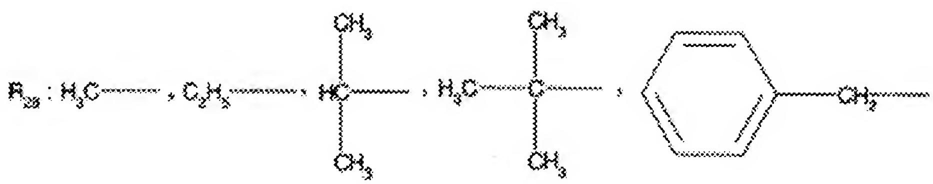
[26] The polyhydroxy alkanoate copolymer according to [25], wherein the 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) is any one of a 3-hydroxy-11-alkoxycarbonylundecanoic acid unit represented by a chemical formula (33):

[0242]

[Chemical Formula 208]



(33)

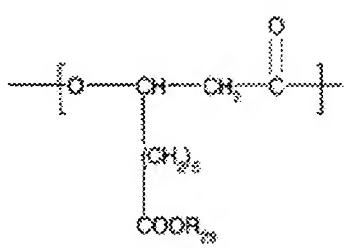


[0243]

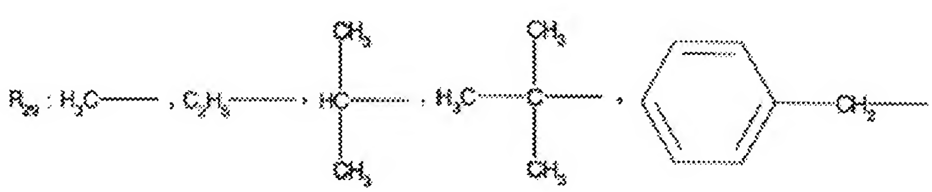
(R_{28} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{28} may be the same or different for each unit), a 3-hydroxy-9-alkoxycarboxynonanoic acid unit represented by a chemical formula (34):

[0244]

[Chemical Formula 209]



(34)



[0245]

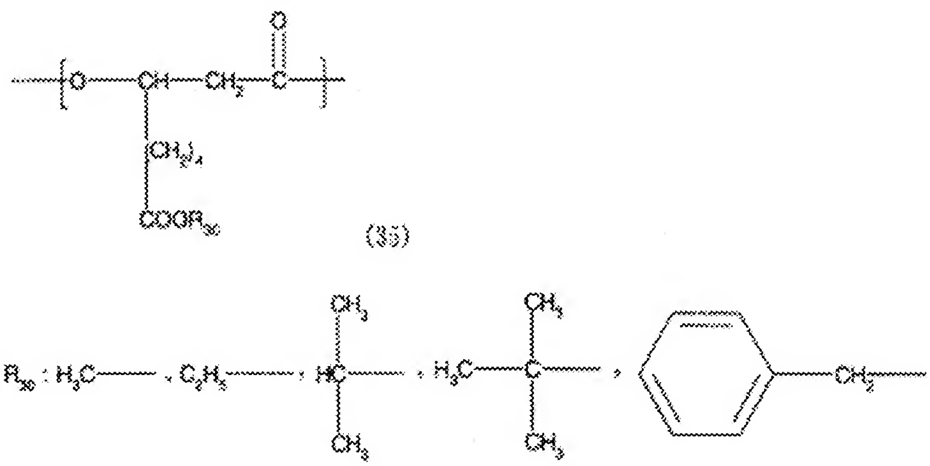
(R_{29} represents any of residues indicated in the

chemical formula; and in case plural units are present, R_{29} may be the same or different for each unit),

a 3-hydroxy-7-alkoxycarboxyheptanoic acid unit represented by a chemical formula (35):

[0246]

[Chemical Formula 210]



(35)

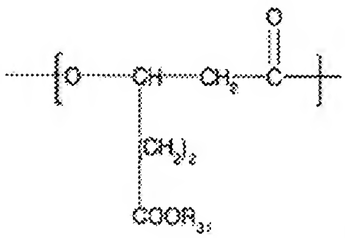
[0247]

(R_{30} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{30} may be the same or different for each unit), and

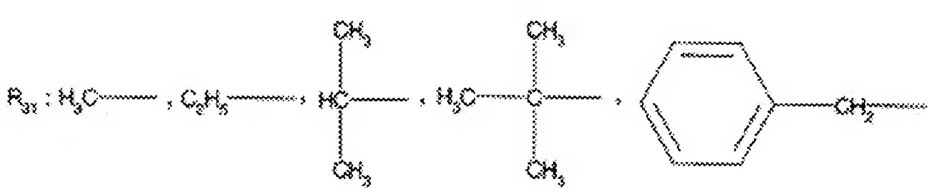
a 3-hydroxy-5-alkoxycarboxyvaleric acid unit represented by a chemical formula (36):

[0248]

[Chemical Formula 211]



(36)



[0249]

(R_{31} represents any of residues indicated in the chemical formula; and in case plural units are present, R_{31} may be the same or different for each unit).

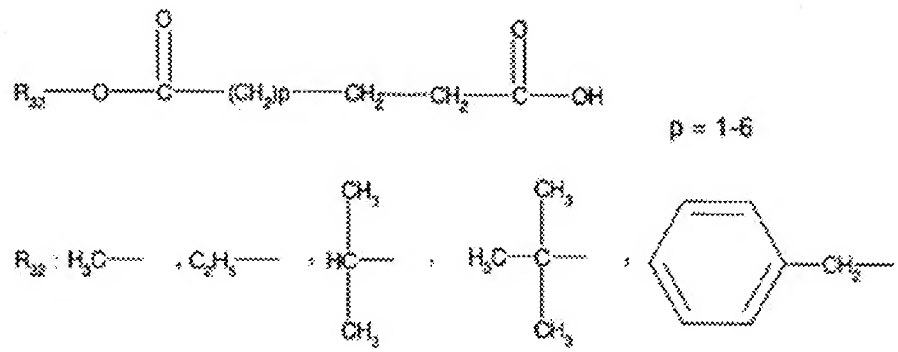
[0250]

[27] The method for producing a polyhydroxy alkanoate copolymer including the 3-hydroxy-ω-carboxyalkanoic acid according to [25] or [26] hydro-synthesized by a microorganism having an ability of producing a polyhydroxy alkanoate copolymer including at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy-ω-alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

from a dicarboxylic acid monoester compound represented by a chemical formula (37):

[0251]

[Chemical Formula 212]



(37)

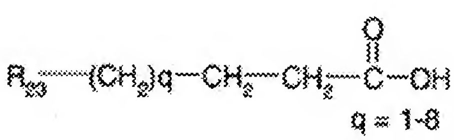
[0252]

in which p represents an integer selected within a range indicated in the chemical formula; and R_{32} represents any of residues indicated in the chemical formula;

and at least a compound represented by a chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by a chemical formula (26) as starting materials:

[0253]

[Chemical Formula 213]



(25)

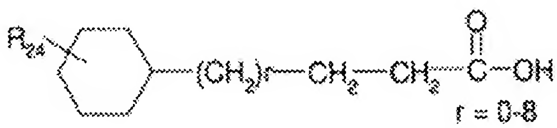
[0254]

in which q represents an integer selected within a range indicated in the chemical formula; and R_{23}

includes a residue having a phenyl structure or a thienyl structure;

[0255]

[Chemical Formula 214]



(26)

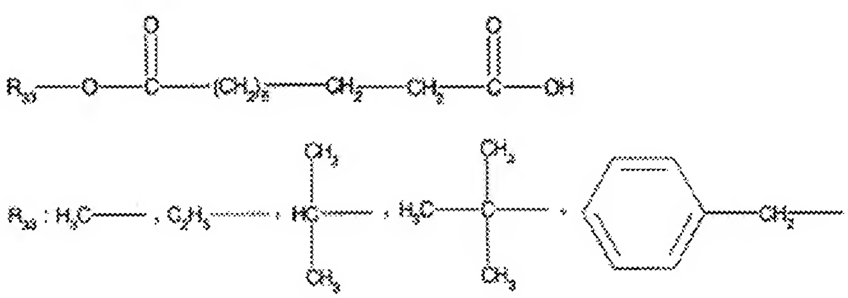
[0256]

in which R_{24} represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula.

[28] The polyhydroxy alkanoate copolymer according to [27], wherein the dicarboxylic acid monoester compound represented by the chemical formula (37) is any one of a sebacic acid monoester compound represented by a chemical formula (38):

[0257]

[Chemical Formula 215]



(38)

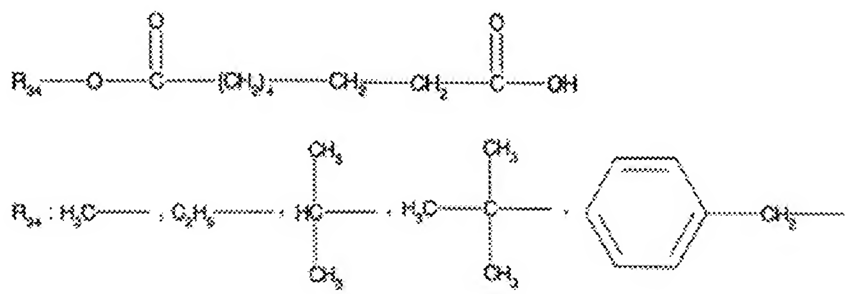
[0258]

(R_{33} represents any of residues indicated in the chemical formula), or

a suberic acid monoester compound represented by a chemical formula (39):

[0259]

[Chemical Formula 216]



(39)

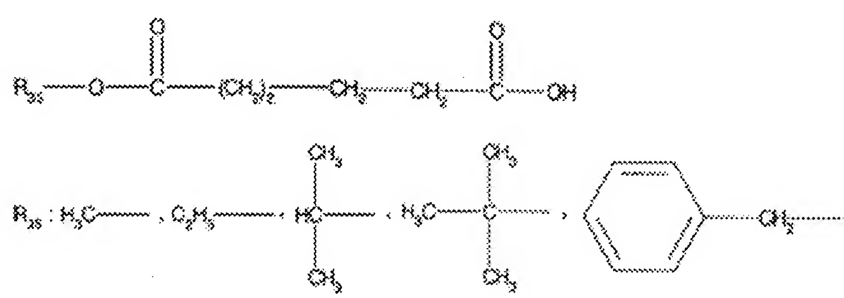
[0260]

(R_{34} represents any of residues indicated in the chemical formula), or

a adipic acid monoester compound represented by a chemical formula (37):

[0261]

[Chemical Formula 217]



(40)

[0262]

(R_{35} represents any of residues indicated in the chemical formula).

[0263]

[29] The method for producing a polyhydroxy alkanoate copolymer including at least the 3-hydroxy-ω-carboxyalkanoic acid according to [27] or [28] in a molecule, which hydro-synthesizes a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) by cultivating a microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by a chemical formula (37), and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by a chemical formula (26).

[0264]

[30] The method for producing a polyhydroxy alkanoate copolymer according to [29], wherein the microorganism is cultured in a culture medium including, in addition to at least a dicarboxylic acid monoester compound represented by the chemical formula (37), and at least a compound represented by the chemical formula (25) or at least a ω-cyclohexylalkanoic acid represented by the chemical formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar, a linear alkanoic acid with 4 to 12 carbon atoms or a

salt thereof.

[0265]

[31] The method for producing a polyhydroxy alkanoate copolymer according to [30], wherein for culturing the organism, the peptide to be added to the culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of piruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; amino acid or salt thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid, aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[0266]

[32] The method for producing a polyhydroxy alkanoate copolymer according to any one of [27] to [31], characterized in including a step of culturing the microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by the chemical formula (37) and at least a compound represented by the chemical formula (25) or at

least an ω-cyclohexylalkanoic acid represented by the chemical formula (26), and recovering a polyhydroxy alkanoate copolymer including simultaneously at least a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) and a 3-hydroxy-ω-alkanoic acid unit represented by the chemical formula (2) or a 3-hydroxy-ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by the microorganism, from cells of the microorganism.

[0267]

[33] The method for producing a polyhydroxy alkanoate copolymer according to [27] to [32], wherein the microorganism is a microorganism belonging to Pseudomonas genus.

[0268]

[34] The method for producing a polyhydroxy alkanoate copolymer according to [33], wherein the microorganism is at least one of Pseudomonas cichorii YN2 strain (FERM BP-7375), Pseudomonas cichorii H45 strain (FERM BP-7374), Pseudomonas jessenii P161 (FERM BP-7376) and `Pseudomonas putida P91 (FERM BP-7373).

[0269]

[35] The method for producing a polyhydroxy alkanoate copolymer according to [25] to [34], wherein R_{25} in the chemical formula (27) and R_{23} in the chemical formula (25), each representing a residue having a

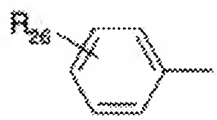
phenyl structure or a thienyl structure, represents at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0270]

the chemical formula (31):

[0271]

[Chemical Formula 218]



(31)

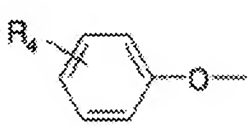
[0272]

represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[0273]

[Chemical Formula 219]



(9)

[0274]

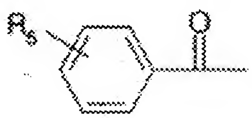
represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen

atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[0275]

[Chemical Formula 220]



(10)

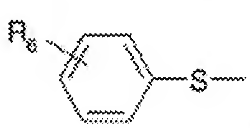
[0276]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0277]

[Chemical Formula 221]



(11)

[0278]

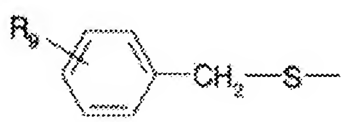
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a

substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0279]

[Chemical Formula 222]



(12)

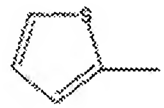
[0280]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0281]

[Chemical Formula 223]



(13)

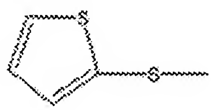
[0282]

represents a 2-thienyl group;

the chemical formula (14):

[0283]

[Chemical Formula 224]



(14)

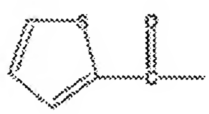
[0284]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0285]

[Chemical Formula 225]



(15)

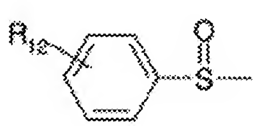
[0286]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0287]

[Chemical Formula 226]



(16)

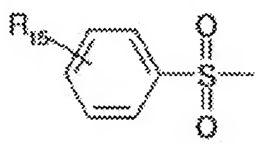
[0288]

represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[0289]

[Chemical Formula 227]



(17)

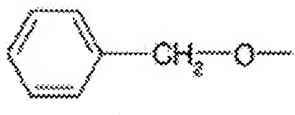
[0290]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2$-CH group or a $(CH_3)_3$-C group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

[0291]

[Chemical Formula 228]



(18)

[0292]

represents a (phenylmethyl)oxy group.

[0293]

The contents of the present invention will be described in details hereinafter.

[0294]

[Embodiment(s)]

A polyhydroxy alkanoate copolymer, the final product of the present invention, is a polyhydroxy alkanoate copolymer (hereinafter also called carboxyl PHA) comprising a unit having a carboxyl group on a side chain as represented by a chemical formula (19) and a unit represented by a chemical formula (2) or a chemical formula (3).

[0295]

The producing methods therefor are mainly classified to:

- a method of oxidizing and cleaving a double bond portion in a polyhydroxy alkanoate copolymer (hereinafter also called a precursor vinyl PHA) including a 3-hydroxy-ω-alkenoic acid unit having a carbon-carbon double bond at an end of a side chain as

represented in a chemical formula (1) and a unit represented by a chemical formula (2) or a chemical formula (3); and

• a method of hydrolyzing an alkoxycarbonyl portion in a polyhydroxy alkanoate copolymer (hereinafter also called an alkoxycarbonyl PHA) including a 3-hydroxy-ω-alkoxyalkanoic acid unit having an ester group at an end of a side chain as represented in a chemical formula (32) and a unit represented by a chemical formula (2) or a chemical formula (3). In the following, the precursor vinyl PHA and the precursor alkoxycarbonyl PHA may be collectively called a precursor PHA.

[0296]

A producing method for such precursor PHA is not particularly restricted, but there can be employed a microbial production using microorganisms, a method using a genetically modified plant, or a chemical polymerization. Preferably a method by microbial production is employed.

[0297]

The precursor vinyl PHA was synthesized for the first time by the present inventors, and the present invention therefore includes also the precursor vinyl PHA itself, and a production process thereof by microorganisms. Also such precursor vinyl PHA can be effectively utilized not only for the carboxyl PHA

which is an object of the present invention but also for introducing other functional groups.

[0298]

In the following, there will be explained a producing method employing each precursor PHA.

[0299]

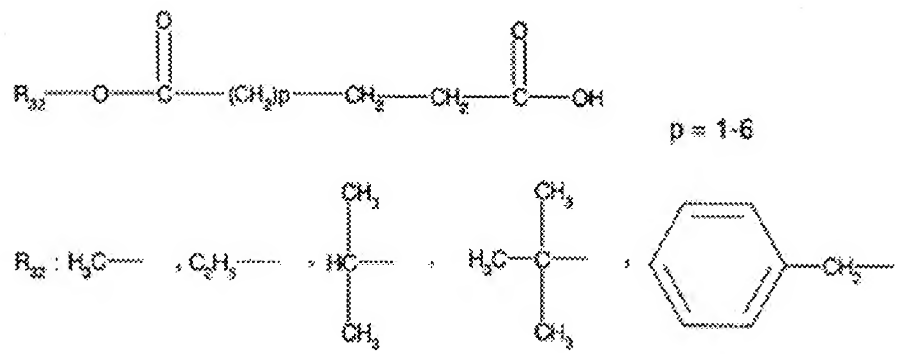
The precursor vinyl PHA can be producing by culturing a microorganism in a culture medium including an ω-alkenoic acid represented by a chemical formula (24) and a compound represented by a chemical formula (25) or an ω-cyclohexylalkanoic acid represented by the chemical formula (26).

[0300]

Similarly, the precursor alkoxycarbonyl PHA can be producing by culturing a microorganism in a culture medium including a carboxylic acid monoester compound represented by a chemical formula (37) and a compound represented by the chemical formula (25) or an ω-cyclohexylalkanoic acid represented by the chemical formula (26).

[0301]

[Chemical Formula 229]



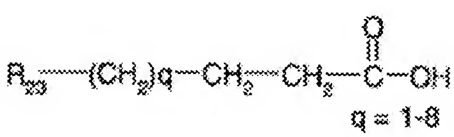
(37)

[0302]

in which p represents an integer selected within a range indicated in the chemical formula; and R_{32} represents any of residues indicated in the chemical formula;

[0303]

[Chemical Formula 230]



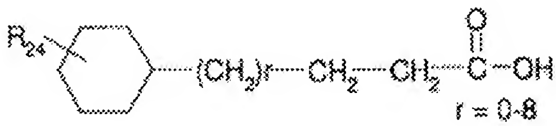
(25)

[0304]

in which q represents an integer selected within a range indicated in the chemical formula; and R_{23} includes a residue having a phenyl structure or a thienyl structure;

[0305]

[Chemical Formula 231]



r = 0-8 (26)

[0306]

in which R_{24} represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula.

More specifically, each precursor PHA can be more advantageously prepared by culturing a microorganism in a culture medium containing respective raw material compounds, namely, for the precursor vinyl PHA, a combination of at least one ω-alkenoic acid represented by the chemical formula (24) and at least one compound represented by the chemical formula (25) or at least one ω-cyclohexylalkanoic acid represented by the chemical formula (26); and for the precursor alkoxycarbonyl PHA, a combination of at least one carboxylic acid monoester compound represented by the chemical formula (37) and at least one compound represented by the chemical formula (25) or at least one ω-cyclohexylalkanoic acid represented by the chemical formula (26), and further containing at least one of peptide, yeast extract, organic acid or salt thereof, amino acid or a salt thereof, sugar, and

linear alkanoic acid with 4 to 12 carbon atoms or salt thereof.

[0307]

As preferable nutrients to be added to the culture medium, the peptide being polypeptone; one or more organic acids selected from a group of piruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; one or more amino acids selected from a group of glutamic acid, aspartic acid and salts thereof; and one or more sugars selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[0308]

In the producing method of the precursor PHA copolymer of the present invention, detailed microbial culture conditions are as follows.

[0309]

The following necessary substrates and nutrients are added to an inorganic salt culture medium based on a phosphate buffer and an ammonium salt or a nitrate salt.

[0310]

The raw material compound for each precursor PHA, namely, for the precursor vinyl PHA, a combination of

at least an ω-alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by the chemical formula (26); or for the precursor alkoxycarbonyl PHA, a combination of at least a carboxylic acid monoester compound represented by the chemical formula (37) and at least a compound represented by the chemical formula (25) or at least an ω-cyclohexylalkanoic acid represented by the chemical formula (26), is preferably contained in the culture medium in a proportion of 0.01 to 1 % (w/v), further preferably 0.02 to 0.2 %.

[0311]

The aforementioned nutrients as a carbon source and a nitrogen source for proliferation, and as an energy source for polyhydroxy alkanoate production are preferably added to the culture medium in a proportion of 0.1 to 5 % (v/v) per medium, more preferably 0.2 to 2 %.

[0312]

It can be employed any inorganic salt culture medium containing a phosphate salt and a nitrogen source such as an ammonium salt or a nitrate salt, but the PHA productivity can be improved by regulating the concentration of the nitrogen source.

[0313]

The culture temperature can be any temperature at

which the microorganism can satisfactorily proliferate, and is usually within a range of 15 to 37°C, preferably 20 to 30°C.

[0314]

The culture may be carried out by any culture method so long as the microorganisms can proliferate and produce PHA, such as a liquid culture or a solid culture. Also it may be batch culture, fed batch culture, semi-continuous culture or continuous culture. For example, for liquid batch culture, the oxygen supply method may be shaking using a shaking flask or agitation aeration in a jar fermenter.

[0315]

In order to make the microorganism produce and accumulate PHA, there can be employed, in addition to the aforementioned method, a method of transferring the cell, after sufficient proliferation, to a culture medium limited in a nitrogen source such as ammonium chloride and to continue culture further in the presence of a compound being a substrate for the desired unit, thereby improving the productivity.

[0316]

Thus the method for producing precursor vinyl PHA of the present invention may comprise the steps of: culturing a production microorganism under the aforementioned conditions, and recovering produced PHA from the cells, the PHA copolymer produced by the

microorganism at least containing a 3-hydroxy-ω-alkenoic acid unit represented by the chemical formula (1), and a unit represented by the chemical formula (2) or an ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule.

[0317]

Also the method for producing precursor alkoxycarbonyl PHA of the present invention may comprise the steps of: culturing a production microorganism under the aforementioned conditions, and recovering from the cells a polyhydroxy alkanoate copolymer produced by the microorganism which at least contains a 3-hydroxy-ω-alkoxycarbonylalkanoic acid unit represented by the chemical formula (32), and a unit represented by the chemical formula (2) or an ω-cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule.

[0318]

The object PHA can be recovered from the cells by an ordinarily employed method. For example, an extraction with an organic solvent such as chloroform, dichloromethane or acetone is most simple, but there may also be employed dioxane, tetrahydrofuran or acetonitrile. Also in a situation where an organic solvent is difficult to use, it is also possible to physically break the cells, for example by treating the cells with a surfactant such as SDS, chemicals such as

hypochlorous acid and EDTA, or with an enzyme such as lysozyme, or by ultrasonic disruption, homogenizer disruption, pressure disruption, beads impulse, grinding or pounding or freeze-and-thawing, to remove cell components other than PHA and recover PHA.

[0319]

A production microorganism to be employed in the production method of the present invention can be any microorganisms having an ability meeting the aforementioned conditions, but there are preferred those belonging to the Pseudomonas genus, and more preferably Pseudomonas cichorii, Pseudomonas putida, Pseudomonas fluorecense, Pseudomonas oleovorans, Pseudomonas aeruginosa, Pseudomonas stutzeri or Pseudomonas jessenii. More specific examples include Pseudomonas cichorii YN2 (FERM BP-7375), Pseudomonas cichorii H45 (FERM BP-7374), Pseudomonas jessenii P161 (FERM BP-7376), and Pseudomonas putida P91 (FERM BP-7373). These four types of strains are deposited on November 20, 2000 at International Patent Organism Depositary, National Institute of Bioscience and Human-Technology, Agency of Industry Science and Technology (independent administrative corporation), Tsukuba Central 6, 1-1, Higashi 1-chome, Tsukuba-shi, Ibaraki-ken 305-8566, Japan, and described in the Japanese Patent Application Laid-Open No. 2002-80571.

[0320]

In the present invention the methods for culture of the microorganism, PHA production and accumulation by the microorganism, and for PHA recovery from the cells are not limited to the methods explained above.

[0321]

The following is a composition of an inorganic salt M9 culture medium employed in the method of the present invention.

[0322]

[M9 culture medium]

Na_2HPO_4	6.3
KH_2PO_4	3.0
NH_4Cl	1.0
NaCl	0.5

(in g/L; pH 7.0)

[0323]

For satisfactory proliferation and resulting PHA production, the above-mentioned inorganic culture medium has to be replenished with the essential trace elements by adding the following trace component solution by about 0.3 % (v/v).

[0324]

[Minor component solution]

Nytrilotriacetic acid	1.5;
$MgSO_4$	3.0;
$MnSO_4$	0.5;
NaCl	1.0;

$FeSO_4$	0.1;
$CaCl_2$	0.1;
$CoCl_2$	0.1;
$ZnSO_4$	0.1;
$CuSO_4$	0.1;
$AlK(SO_4)_2$	0.1;
H_3BO_3	0.1;
Na_2MoO_4	0.1;
$NiCl_2$	0.1;

(in g/L).

[0325]

The polyhydroxy alkanoates synthesized by the aforementioned producing method, a polyhydroxy alkanoate copolymer including a unit represented by the chemical formula (1) and a unit represented by the chemical formula (2) or a unit represented by the chemical formula (3) can be oxidized at the carbon-carbon double bond portion to give a polyhydroxy alkanoate copolymer including a unit represented by the chemical formula (19), and a unit represented by the chemical formula (2) or a unit represented by the chemical formula (3). For obtaining a carboxylic acid by oxidizing a carbon-carbon double bond with an oxidant, there are known, for example, a method of utilizing a permanganate salt (J. Chem. Soc. Perkin. Trans. 1, 806 (1973); Non-patent Document 16)); a method of utilizing a bichromate salt (Org. Synth., 4,

698 (1963); Non-patent Document 17); a method of utilizing a periodate salt (J. Org. Chem., 46, 19 (1981); Non-patent Document 18); a method of utilizing nitric acid (Japanese Patent Application Laid-Open No. S59-190945; Patent Document 9); a method of utilizing ozone (J. Am. Chem. Soc., 81, 4273 (1959); Non-patent Document 19) etc., and, on polyhydroxy alkanoate, Macromolecular chemistry, 4, 289-293 (2001) (Non-patent Document 14) reports a method of obtaining a carboxylic acid by oxidizing the carbon-carbon double bond at the end of the side chain of polyhydroxy alkanoate with potassium permanganate as an oxidant and under an acidic condition. A similar method can be utilized also in the present invention.

[0326]

The oxidant to be employed in the present invention, though not particularly limited, is preferably a permanganate salt. Such permanganate salt to be employed as the oxidant is usually potassium permanganate. Since the oxidation reaction is a stoichiometric reaction, the amount of the permanganate salt is usually 1 molar equivalent or more with respect to 1 mole of the unit represented by the chemical formula (1), preferably 2 to 10 molar equivalents.

[0327]

For executing the reaction under an acidic condition, there is usually employed an inorganic acid

such as sulfuric acid, hydrochloric acid, acetic acid or nitric acid, or an organic acid. However the use of sulfuric acid, nitric acid or hydrochloric acid may cause cleavage of an ester bond in the main chain of polyhydroxy alkanoate, thereby resulting in a decrease in the molecular weight. It is therefore preferable to employ acetic acid. An amount of acid is usually within a range of 0.2 to 200 molar equivalents per 1 mole of the unit represented by the chemical formula (1), preferably 0.4 to 100 molar equivalents. An amount less than 0.2 molar equivalents results in a low yield, while an amount exceeding 200 molar equivalents generates by-products by decomposition with acid. Also a crown ether may be employed for the purpose of accelerating the reaction. In this case, crown ether and permanganate salt form a complex, thereby providing an effect of increasing the reaction activity. As the crown ether, there is generally employed dibenzo-18-crown-6-ether, dicyclo-18-crown-6-ether, or 18-crown-6-ether. An amount of crown ether is generally within a range of 0.5 to 2.0 molar equivalents per 1 mole of permanganate salt, preferably 0.5 to 1.5 molar equivalents.

[0328]

As a solvent to be employed in the oxidation and cleavage reaction of the present invention, there may be employed any solvent inert to the reaction without

particular limitation, for example water, acetone; an ether such as tetrahydrofuran or dioxane; an aromatic hydrocarbon such as benzene; an aliphatic hydrocarbon such as hexane or heptane; or a halogenated hydrocarbon such as methyl chloride, dichloromethane or chloroform. Among these solvents, in consideration of dissolving property for polyydroxy alkanoate, a halogenated hydrocarbon such as methyl chloride, dichloromethane or chloroform, or acetone is preferred.

[0329]

In the aforementioned oxidation and cleavage reaction of the present invention, a precursor vinyl PHA, a permanganate salt and an acid may be introduced into a solvent at a time from the beginning and reacted together, or they may be added to the reaction system one by one continuously or intermittently to be reacted. Or first a permanganate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a polyhydroxyalkanoate and an acid to the reaction system, or first a polyhydroxyalkanoate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a permanganate and an acid to the reaction system. Further, first a polyhydroxyalkanoate and an acid are introduced into a solvent and then a permanganate is added to the reaction system continuously or intermittently to be reacted, or first permanganate and an acid are

introduced into a solvent and then polyhydroxyalkanoate is added to the reaction system continuously or intermittently, or first a polyhydroxyalkanoate and a permanganate are introduced into a solvent and then an acid is added to the reaction system continuously and intermittently to be reacted.

[0330]

A reaction temperature is selected generally within a range from -40 to 40°C, preferably -10 to 30°C. A reaction time depends on a stoichiometric ratio of the unit represented by the chemical formula (1) and permanganate salt and the reaction temperature, but is generally selected within a range of 2 to 48 hours.

Also in the oxidation and cleavage reaction of the present invention, in case R_2 in the unit represented by the chemical formula (2) is a residue represented by the chemical formula (11), a sulfide bond therein may be converted into a sulfoxide or a sulfone.

[0331]

Next, there will be explained the producing method of the precursor ester PHA of the present invention employing, as a starting material, a polyhydroxy alkanoate copolymer including a unit represented by the chemical formula (32), and a unit represented by a chemical formula (2) or a unit represented by a chemical formula (3).

[0332]

A precursor ester PHA synthesized can provide the carboxyl PHA by hydrolysis in the presence of an acid or an alkali or hydrogenolysis including catalytic reduction of an ester bond portion shown in the chemical formula (48). Such method of hydrolysis in the presence of an acid or an alkali can be carried out by employing, in a water-miscible organic solvent such as methanol, ethanol, tetrahydrofuran, dioxane, dimethylformamide or dimethylsulfoxide, an aqueous solution or an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid; an organic acid such as trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid or methanesulfonic acid; an aqueous caustic alkali such as sodium hydroxide or potassium hydroxide; an aqueous solution or an alkali carbonate such as sodium carbonate or potassium carbonate; or an alcoholic solution of a metal alkoxide such as sodium methoxide or sodium ethoxide. The reaction temperature is selected ordinarily from 0 to 40°C, preferably from 0 to 30°C. The reaction period is ordinarily selected from 0.5 to 48 hours. However, a hydrolysis with an acid or an alkali may also cause a cleavage of an ester bonding of the main molecular chain, thereby resulting in a decrease in the molecular weight.

[0333]

Also the method of obtaining a carboxylic acid by

hydrogenolysis including catalytic reduction is carried out in the following manner. Catalytic reduction is carried out in a suitable solvent and within a temperature range from -20°C to the boiling point of the used solvent, preferably from 0 to 50°C, by reacting hydrogen under a normal pressure or an elevated pressure in the presence of a reducing catalyst. Examples of the usable solvent include water, methanol, ethanol, propanol, ethyl acetate, diethyl ether, tetrahydrofuran, dioxane, benzene, toluene, dimethylformamide and pyridine. In consideration of the solubility, tetrahydrofuran, toluene or dimethylformamide is particularly preferable. As the reducing catalyst, there can be employed palladium, platinum or rhodium either singly or held on a carrier, or Raney nickel. However, the catalytic reduction may also cause cleavage of an ester bonding of the main molecular chain to decrease the molecular weight.

[0334]

In the following, the present invention will be explained in more details by examples thereof. These examples represent examples of the optimum embodiments of the present invention, but the present invention is by no means limited by these examples.

[0335]

[Examples]

[Example 1]

0.5% of polypeptone (supplied by Wako Pure Chemical Co.), 6 mmol/L of 5-phenoxyvaleric acid, and 1 mmol/L of 10-undecenoic acid were dissolved in 200 ml of an aforementioned M9 culture medium, which was placed in a 200 ml shaking flask, then sterilized in an autoclave and cooled to the room temperature. Then 2 ml of a culture liquid of Pseudomonas cichorii YN2, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours at 30°C, was added to the prepared culture medium, and culture was conducted for 64 hours at 30°C. After the culture, the cells were collected by centrifugation, washed with methanol and dried. The dried cells, after weighing, were put in chloroform and stirred for 72 hours at 35°C to extract a polymer. The chloroform extract was filtered, then concentrated on an evaporator, and a solid precipitate formed by an addition of cold methanol was collected and dried under a reduced pressure to obtain a desired polymer.

[0336]

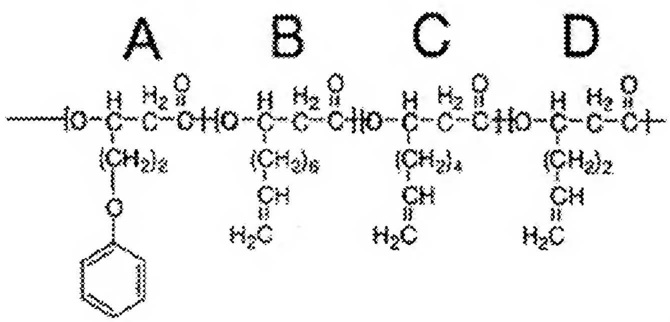
Structure of the obtained polymer was determined by ^{1}H-NMR (FT-NMR: Bruker DPX400; ^{1}H resonance frequency: 400 MHz; measured nucleus species: ^{1}H; solvent: $CDCl_3$; reference: capillary-sealed TMS/$CDCl_3$; measurement temperature: room temperature).

Fig. 1 shows a ^{1}H-NMR spectrum of the obtained polymer. As a result, the obtained polymer was

confirmed being a polyhydroxy alkanoate copolymer including a unit represented by the following chemical formula (41) (A : B+C+D : others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) = 87 : 9 : 4). Also ^{13}C-NMR confirmed presence of the unit B which is a 3-hydroxy-10-undecenoic acid unit and both of the unit C which is a 3-hydroxy-8-nonenoic acid unit and the unit D which is a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0337]

[Chemical Formula 232]



(41)

[0338]

The molecular weight of the obtained polymer was measured by gel permeation chromatography (GPC) (Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, molecular weight converted into polystyrene).

[0339]

The obtained polymer dry weight (PDW) was 0.19 g/L and the number-averaged molecular weight was 30,000.

[0340]

[Example 2]

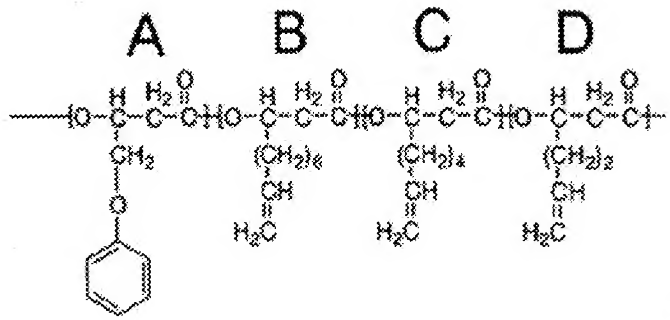
A desired polymer was obtained in the same manner as in Example 1, except that 5-phenoxyvaleric acid employed in Example 1 was changed to 4-phenoxybutyric acid.

[0341]

Structure of the obtained polymer was determined by ^{1}H-NMR and ^{13}C-NMR as in Example 1. Fig. 1 shows a 1H-NMR spectrum of the obtained polymer. As a result, the obtained polymer was confirmed being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (42) (A : B+C+D : others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) = 72 : 11 : 15). Also ^{13}C-NMR confirmed the presence of the unit B which is a 3-hydroxy-10-undecenoic acid unit and both of the unit C which is a 3-hydroxy-8-nonenoic acid unit and the unit D which is a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0342]

[Chemical Formula 233]



(42)

[0343]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0344]

The obtained polymer weighed (PDW) 0.05 g/L and a number-averaged molecular weight was 25,000.

[0345]

[Example 3]

A desired polymer was obtained in the same manner as in Example 1, except that 5-phenoxyvaleric acid employed in Example 1 was changed to 4-cyclohexylbutyric acid.

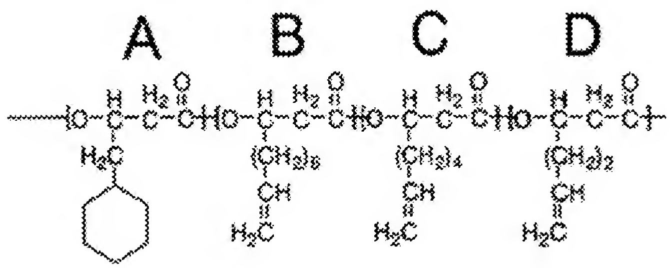
[0346]

Structure of the obtained polymer obtained by ^{1}H-NMR and ^{13}C-NMR as in Example 1 was determined to confirm that the polyhydroxy alkanoate copolymer includes units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 89 : 11).

Also ^{13}C-NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0347]

[Chemical Formula 234]



(43)

[0348]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0349]

The obtained polymer weighed (PDW) 0.52 g/L and the number-averaged molecular weight was 154,000.

[0350]

[Example 4]

A desired polymer was obtained in the same manner as in Example 3, except that polypeptone employed in Example 3 was changed to yeast extract.

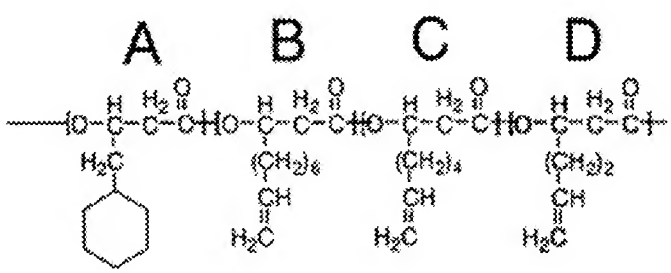
[0351]

Structure of the obtained polymer was determined by ^{1}H-NMR and ^{13}C-NMR as in Example 1 to confirm the

polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 85 : 15). Also ^{13}C-NMR confirmed the presence of the unit B is a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0352]

[Chemical Formula 235]



(43)

[0353]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0354]

The obtained polymer weighed (PDW) 0.45 g/L and the number-averaged molecular weight was 132,000.

[0355]

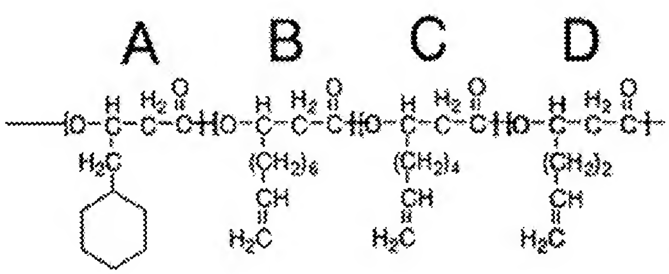
[Example 5]

A polymer was obtained in the same manner as in

Example 3, except that the strain YN2 employed in Example 3 was replaced by Pseudomonas cichorii H45 and polypeptone was changed to glucose. Structure of the obtained polymer was determined by ^{1}H-NMR and ^{13}C-NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 83 : 17). Also ^{13}C-NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0356]

[Chemical Formula 236]



(43)

[0357]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0358]

The obtained polymer weighed (PDW) 0.41 g/L and the number-averaged molecular weight was 164,000.

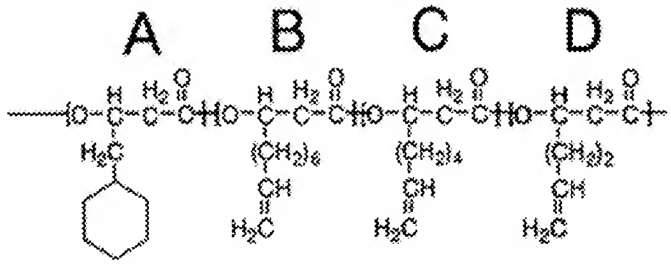
[0359]

[Example 6]

A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by Pseudomonas cichorii H45 and polypeptone was changed to sodium pyruvate. A structure determination of the obtained polymer was conducted by ^{1}H-NMR and ^{13}C-NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 87 : 13). Also ^{13}C-NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0360]

[Chemical Formula 237]



(43)

[0361]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0362]

The weight of the obtained polymer (PDW) was 0.28 g/L and the number-averaged molecular weight was 156,000.

[0363]

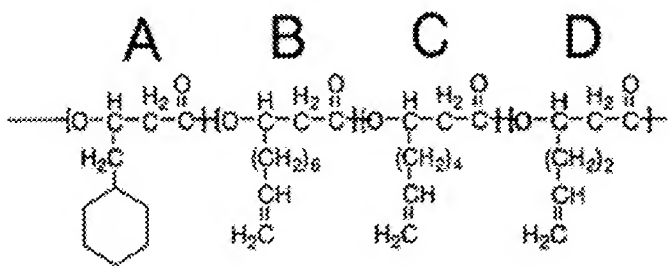
[Example 7]

A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by Pseudomonas jessenii P161 and polypeptone was changed to sodium glutamate. Structure determination of the obtained polymer was conducted by ^{1}H-NMR and ^{13}C-NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 88 : 12). Also ^{13}C-NMR confirmed the presence of the unit B being

a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0364]

[Chemical formula 238]



(43)

[0365]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0366]

The weight of the obtained polymer (PDW) was 0.38 g/L and the number-averaged molecular weight of 145,000.

[0367]

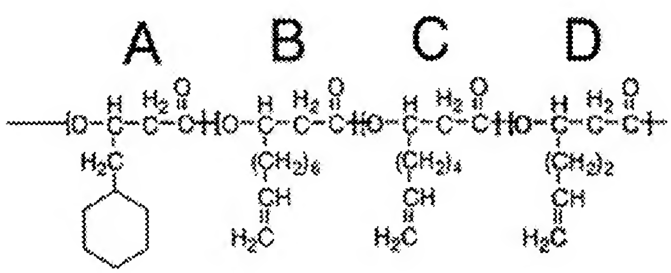
[Example 8]

A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by Pseudomonas jessenii P161 and 0.5% polypeptone was changed to 0.1% of nonanic acid. The structure determination of the obtained polymer was conducted by ^{1}H-NMR and ^{13}C-NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate

copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 80 : 20). Also ^{13}C-NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0368]

[Chemical Formula 239]



(43)

[0369]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0370]

The weight of the obtained polymer (PDW) was 0.18 g/L and the number-averaged molecular weight was 132,000.

[0371]

[Example 9]

Twenty 200 ml shaking flasks were prepared, into which 0.5% of polypeptone (supplied by Wako Pure Chemical Co.), 6 mmol/L of 5-phenoxyvaleric acid, and 1 mmol/L of 10-undecenoic acid dissolved in 200 ml of an aforementioned M9 culture medium was placed, then sterilized in an autoclave and cooled to the room temperature. Then 2 ml of a culture liquid of Pseudomonas cichorii YN2, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours at 30°C, was added to each flask, and culture was conducted for 64 hours at 30°C. After the culture, all cells were collected by centrifugation, washed with methanol and dried. The dried cells, after weighing, were put in chloroform and stirred for 72 hours at 25°C to extract a polymer. The chloroform extract was filtered, then concentrated on an evaporator, and a solid precipitate formed by an addition of cold methanol was collected and dried under a reduced pressure to obtain a desired polymer.

[0372]

The obtained PHA polymer weighed 1528 mg (dry weight) in the present example.

[0373]

The average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a

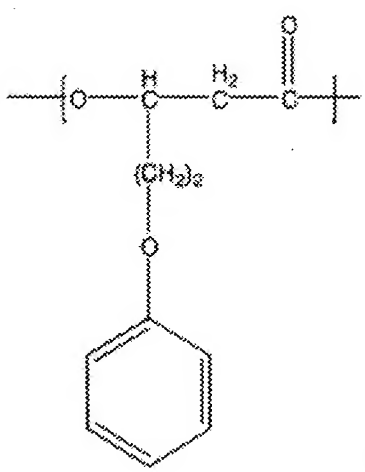
result there were obtained a number-averaged molecular weight Mn = 104000 and a weight-averaged molecular weight Mw = 231000. The structure of the obtained polymer was determined by ^{1}H-NMR and ^{13}C-NMR as in Example 1.

[0374]

As a result, confirmed was a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-phenoxyvaleric acid represented by the following chemical formula (44), 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-nonenoic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenoic acid represented by a chemical formula (7).

[0375]

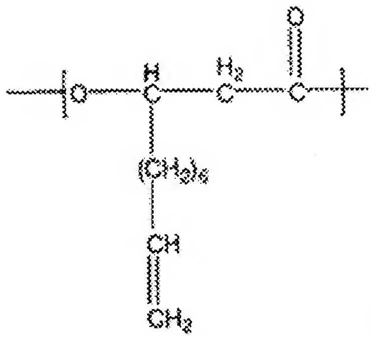
[Chemical Formula 240]



(44)

[0376]

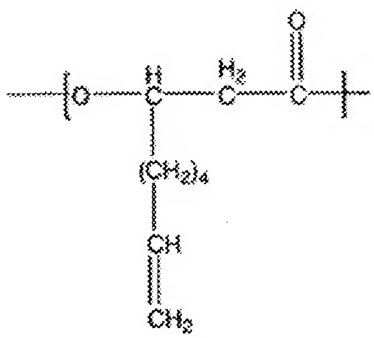
[Chemical Formula 241]



(5)

[0377]

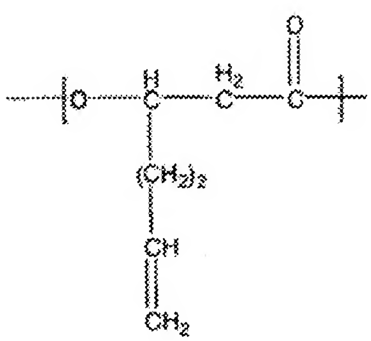
[Chemical Formula 242]



(6)

[0378]

[Chemical Formula 243]



(7)

[0379]

The proportion of such units confirmed by ^{1}H-NMR was: 69 mol% of 3-hydroxy-5-phenoxyvaleric acid, 23

mol% of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenoic acid and 3-hydroxy-6-heptenoic acid in total, and 8 mol% of others (linear 3-hydroxyalkanoic acids of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acids with 10 or 12 carbon atoms).

[0380]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction.

[0381]

303 mg of polyhydroxy alkanoate were charged in a 200-ml eggplant-shaped flask and were dissolved by adding 20 ml of dichloromethane. The solution was placed in an iced bath, and 3 ml of acetic acid and 300 mg of 18-crown-6-ether were added and agitated. Then, in an iced bath, 241 mg of potassium permanganate were slowly added and an agitation was carried out for 20 hours at the room temperature. After the reaction, 50 ml of water and 500 mg of sodium bisulfite were added. Then the liquid was brought to pH = 1 by 1.0 N hydrochloric acid. After dichloromethane in the mixed solvent was distilled off in an evaporator, a polymer in the solution was recovered. The polymer was recovered by washing with 100 ml of methanol and washing three times with 100 ml of purified water. A drying under a reduced pressure provided 247 mg of the desired PHA.

[0382]

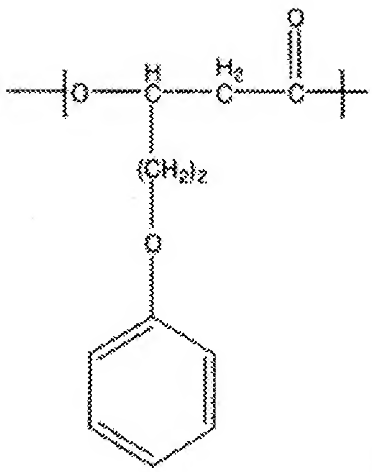
An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a result there were obtained a number-averaged molecular weight Mn = 29400 and a weight-averaged molecular weight Mw = 102800.

[0383]

A structure determination of the obtained polymer carried out by ^{1}H-NMR and ^{13}C-NMR as in Example 1 confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-phenoxyvaleric acid represented by the following chemical formula (44), 3-hydroxy-9-carboxynonanoic acid represented by a chemical formula (45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy-5-carboxyvaleric acid represented by a chemical formula (47).

[0384]

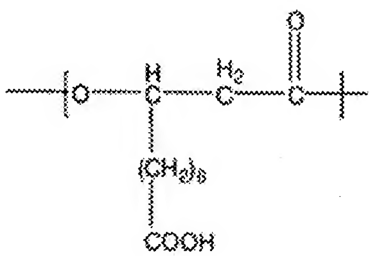
[Chemical Formula 244]



(44)

[0385]

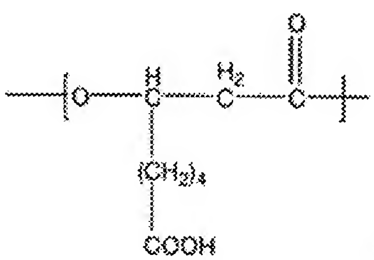
[Chemical Formula 245]



(45)

[0386]

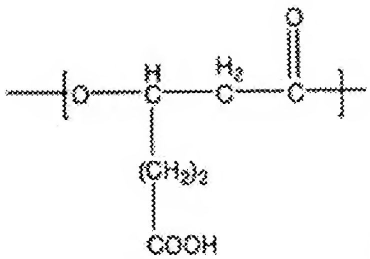
[Chemical Formula 246]



(46)

[0387]

[Chemical Formula 247]



(47)

[0388]

Also a proportion of the units of the obtained PHA was calculated by a methylesterification, utilizing trimethylsilyldiazomethane, of a carboxyl group at an end of a side chain of the PHA.

[0389]

50 mg of the object PHA were charged in a 100-ml eggplant-shaped flask and were dissolved by adding 3.5 ml of chloroform and 0.7 ml of methanol. The solution was added with 2 ml of a 0.63 mol/L solution of trimethylsilyldiazomethane in hexane (supplied by Tokyo Kasei Co.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided 49 mg of PHA.

[0390]

NMR analysis as mentioned above confirmed a proportion of the units in which 3-hydroxy-5-phenoxyvaleric acid was present by 83 mol%, a sum of

three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-heptanoic acid and 3-hydroxy-5-valeric acid by 8 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 9 mol%.

[0391]

[Example 10]

There were prepared twenty 500-ml shake flasks, and, in each, 0.5 wt.% of polypeptone (supplied by Wako Pure Chemical Co.), 6 mmol/L of 4-cyclohexylbutyric acid, and 3 mmol/L of 10-undecenoic acid were dissolved in 200 ml of an aforementioned M9 culture medium, which was placed in a 500 ml shake flask, then sterilized in an autoclave and cooled to the room temperature. Then 2 ml of a culture liquid of Pseudomonas cichorii YN2 strain, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours, was added to each prepared culture medium, and culture was conducted for 60 hours at 30°C. After the culture, the culture liquids were united, and the cells were recovered by centrifuging, rinsed with methanol and dried. The dried cells, after weighing, were agitated with chloroform for 72 hours at 25°C to extract a polymer. The chloroform extract was filtered with a 0.45 μm membrane filter, then concentrated in an evaporator, and the polymer was recovered by a reprecipitation in cold methanol. A desired polymer

was then obtained by drying under a reduced pressure.

[0392]

According to a weighing of the obtained polymer, 1433 mg (dry weight) of PHA were obtained in the present example.

[0393]

An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a result there were obtained a number-averaged molecular weight Mn = 143000 and a weight-averaged molecular weight Mw = 458000.

[0394]

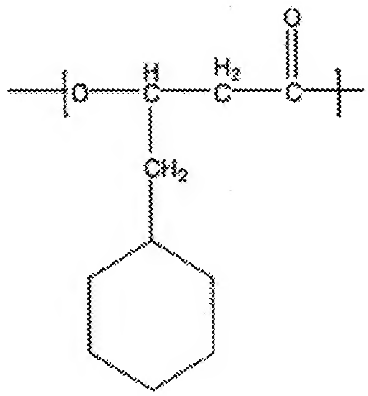
A structure of the obtained PHA was determined by a NMR analysis as in Example 1.

[0395]

As a result, there was confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-cyclohexylbutyric acid represented by the following chemical formula (48), 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-nonenoic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenoic acid represented by a chemical formula (7).

[0396]

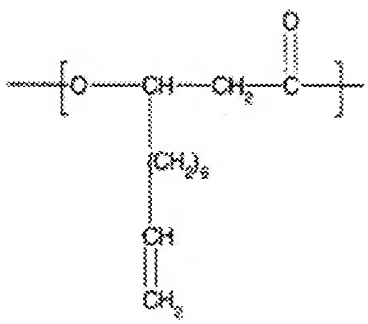
[Chemical Formula 248]



(48)

[0397]

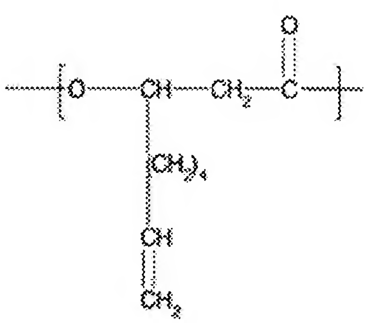
[Chemical Formula 249]



(5)

[0398]

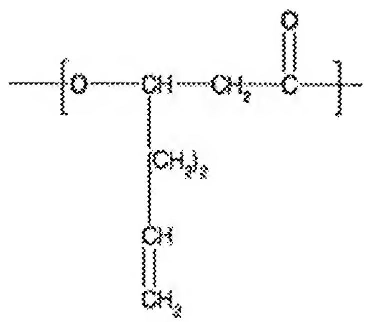
[Chemical Formula 250]



(6)

[0399]

[Chemical Formula 251]



(7)

[0400]

Also a proportion of such units was confirmed by ^{1}H-NMR spectrum, where a sum of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenoic acid and 3-hydroxy-6-heptenoic acid was present by 37 mol%, and 3-hydroxy-4-cyclohexylbutyric acid and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 63 mol%.

[0401]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction.

[0402]

301 mg of polyhydroxy alkanoate were charged in a 200-ml eggplant-shaped flask and were dissolved by adding 20 ml of dichloromethane. The solution was placed in an iced bath, and 3 ml of acetic acid and 541 mg of 18-crown-6-ether were added and agitated. Then, in an iced bath, 430 mg of potassium permanganate were slowly added and an agitation was carried out for 20 hours at the room temperature. After the reaction, 50

ml of water and 1000 mg of sodium bisulfite were added. Then the liquid was brought to pH = 1 by 1.0 N hydrochloric acid. After dichloromethane in the mixed solvent was distilled off in an evaporator, a polymer in the solution was recovered. The polymer was recovered by washing with 100 ml of methanol and washing three times with 100 ml of purified water. A drying under a reduced pressure provided 184 mg of the desired PHA.

[0403]

An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a result there were obtained a number-averaged molecular weight Mn = 111800 and a weight-averaged molecular weight Mw = 272800.

[0404]

For specifying the structure of the obtained PHA, a NMR analysis was carried out under conditions same as in Example 1.

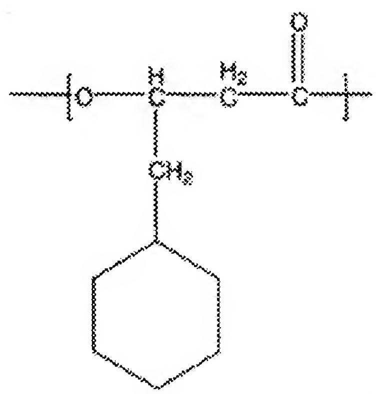
[0405]

As a result, there was confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-4-cyclohexylvaleric acid represented by the following chemical formula (48), 3-hydroxy-9-carboxynonanoic acid represented by a chemical formula

(45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy-5-carboxyvaleric acid represented by a chemical formula (47).

[0406]

[Chemical Formula 252]



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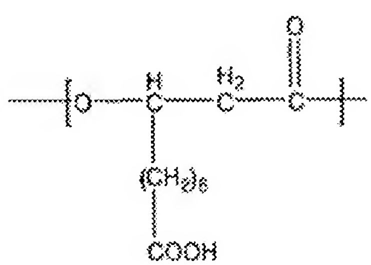
[0407]

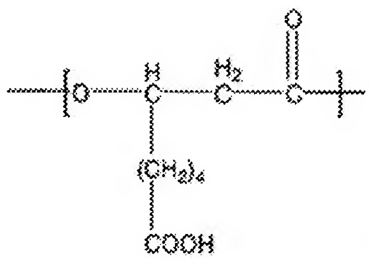
[Chemical Formula 253]



(45)

[0408]

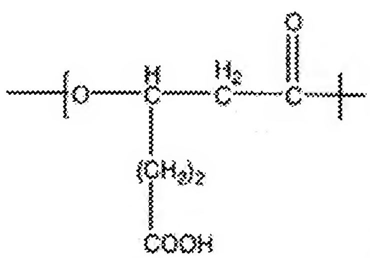
[Chemical Formula 254]



(46)

[0409]

[Chemical Formula 255]



(47)

[0410]

Also a proportion of the units of the obtained PHA was calculated by a methylesterification, utilizing trimethylsilyldiazomethane, of a carboxyl group at an end of a side chain of the PHA.

[0411]

30 mg of the object PHA were charged in a 100-ml eggplant-shaped flask and were dissolved by adding 2.1 ml of chloroform and 0.4 ml of methanol. The solution was added with 0.9 ml of a 0.63 mol/L solution of trimethylsilyldiazomethane in hexane (supplied by Tokyo Kasei Co.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided 31 mg of PHA.

[0412]

A NMR analysis was carried out as mentioned above. As a result, ^1H-NMR spectrum confirmed a proportion of the units in which a sum of three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-carboxyheptanoic acid and 3-hydroxy-5-carboxyvaleric acid was present by 9 mol%, and 3-hydroxy-4-cyclohexyl butyric acid and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 91 mol%.

[0413]

[Example 11]

There were prepared three 2000-ml shake flasks, and, in each, 0.5 wt.% of polypeptone (supplied by Wako Pure Chemical Co.), 4.8 mmol/L of 5-(phenylsulfanyl)valeric acid, and 2 mmol/L of 10-undecenoic acid were dissolved in 1000 ml of an aforementioned M9 culture medium, which was placed in a 2000 ml shake flask, then sterilized in an autoclave and cooled to the room temperature. Then 10 ml of a culture liquid of Pseudomonas cichorii YN2 strain, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours, was added to each prepared culture medium, and culture was

conducted for 38 hours at 30°C. After the culture, the culture liquids were united, and the cells were recovered by centrifuging, rinsed with methanol and dried. The dried cells, after weighing, were agitated with chloroform for 25 hours at 35°C to extract a polymer. The chloroform extract was filtered with a 0.45 μm membrane filter, then concentrated in an evaporator, and the polymer was recovered by a reprecipitation in cold methanol. A desired polymer was then obtained by drying under a reduced pressure.

[0414]

According to a weighing of the obtained polymer, 1934 mg (dry weight) of PHA were obtained in the present example.

[0415]

An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a result there were obtained a number-averaged molecular weight Mn = 430000 and a weight-averaged molecular weight Mw = 150000.

[0416]

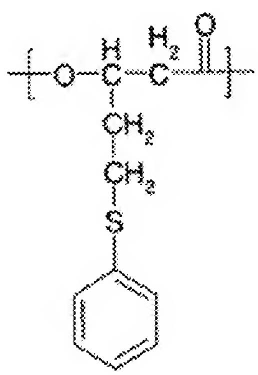
A structure of the obtained PHA was determined by a NMR analysis as in Example 1. An obtained ^{1}H-NMR spectrum is shown in Fig. 3.

[0417]

As a result, there was confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-(phenylsulfanyl)valeric acid represented by the following chemical formula (49), 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-nonenoic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenoic acid represented by a chemical formula (7).

[0418]

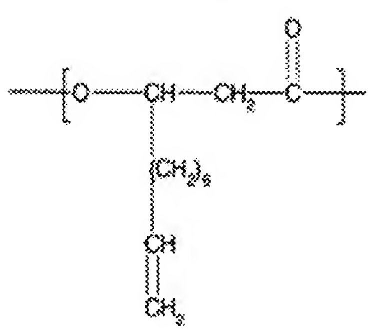
[Chemical Formula 256]



(49)

[0419]

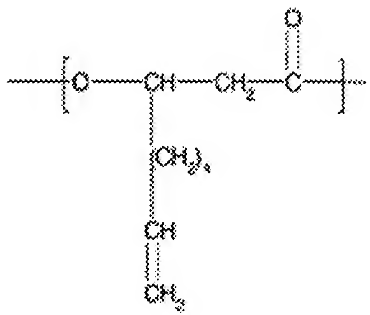
[Chemical Formula 257]



(5)

[0420]

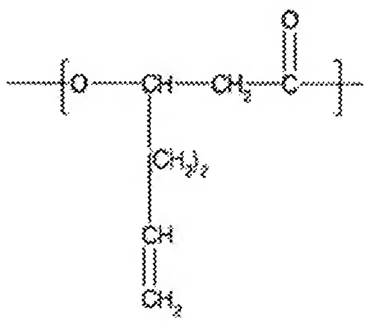
[Chemical Formula 258]



(6)

[0421]

[Chemical Formula 259]



(7)

[0422]

Also a proportion of such units was confirmed by ^{1}H-NMR spectrum, where 3-hydroxy-5-(phenylsulfanyl)valeric acid was present by 78 mol%, a sum of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenoic acid and 3-hydroxy-6-heptenoic acid by 19 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 3 mol%.

[0423]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction. 302 mg of

polyhydroxy alkanoate were charged in a 200-ml eggplant-shaped flask and were dissolved by adding 20 ml of dichloromethane. The solution was placed in an iced bath, and 3 ml of acetic acid and 1154 mg of 18-crown-6-ether were added and agitated. Then, in an iced bath, 917 mg of potassium permanganate were slowly added and an agitation was carried out for 19 hours at the room temperature. After the reaction, 50 ml of water and 3010 mg of sodium bisulfite were added. Then the liquid was brought to pH = 1 by 1.0 N hydrochloric acid. After dichloromethane in the mixed solvent was distilled off in an evaporator, a polymer in the solution was recovered. The polymer was recovered by washing with 100 ml of methanol and washing three times with 100 ml of purified water. A drying under a reduced pressure provided 311 mg of the desired PHA.

[0424]

An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a result there were obtained a number-averaged molecular weight Mn = 62000 and a weight-averaged molecular weight Mw = 260000.

[0425]

For specifying the structure of the obtained PHA, a NMR analysis was carried out under conditions same as

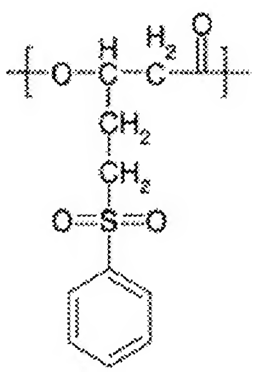
in Example 1. An obtained [1]H-NMR spectrum is shown in Fig. 4.

[0426]

As a result, there was confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-(phenylsulfonyl)valeric acid represented by the following chemical formula (50), 3-hydroxy-9-carboxynonanoic acid represented by a chemical formula (45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy-5-carboxyvaleric acid represented by a chemical formula (47).

[0427]

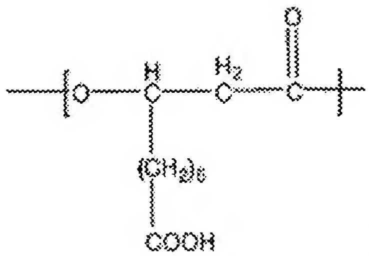
[Chemical Formula 260]



(50)

[0428]

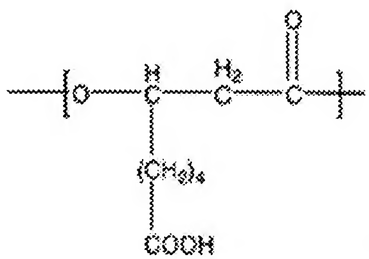
[Chemical Formula 261]



(45)

[0429]

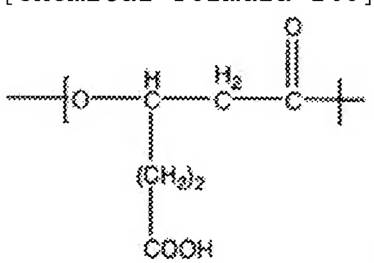
[Chemical Formula 262]



(46)

[0430]

[Chemical Formula 263]



(47)

[0431]

Also a proportion of the units of the obtained PHA was calculated by a methylesterification, utilizing trimethylsilyldiazomethane, of a carboxyl group at an end of a side chain of the PHA.

[0432]

30 mg of the object PHA were charged in a 100-ml

eggplant-shaped flask and were dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. The solution was added with 0.5 ml of a 2 mol/L solution of trimethylsilyldiazomethane in hexane (supplied by Aldrich Inc.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided 31 mg of PHA.

[0433]

A NMR analysis was carried out as in Example 1. As a result, ^{1}H-NMR spectrum confirmed a proportion of the units in which 3-hydroxy-5-(phenylsulfonyl)valeric acid was present by 89 mol%, a sum of three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-carboxyheptanoic acid and 3-hydroxy-5-carboxyvaleric acid by 8 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 3 mol%.

[0434]

[Effect of the Invention]

The method of the present invention provides a novel polyhydroxy alkanoate copolymer including a unit having a vinyl group in a side chain and a unit including a residue having any of a phenyl structure, a thienyl strucrure, and a cyclohexyl structure in the

side chain simultaneously.

[0435]

The present invention further provides a method for producing PHA such that PHA can be produced at a high yield, the unit ratio of the side chain having a vinyl group can be controlled, and physical properties of PHA thus produced can be regulated. The present invention provides a polyhydroxy alkanoate copolymer including a monomer unit having a carboxyl group at the end of a side chain and unusual PHA having on the side chain thereof a substituent other than a linear alkyl group, such as a phenyl structure, a thienyl structure or a cyclohexyl structure, and a producing method therefor.

[Brief Description of the Drawings]

[Fig. 1] A ^{1}H-NMR spectrum of a polyester obtained in Example 1.

[Fig. 2] A ^{1}H-NMR spectrum of a polyester obtained in Example 2.

[Fig. 3] A ^{1}H-NMR spectrum of a polyhydroxy alkanoate copolymer obtained in Example 11, and including 3-hydroxy-5-(phenylsulfanyl)valeric acid represented by a chemical formula (49), a 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-noneic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenic acid represented by a chemical formula (7).

[Fig. 4] A ^{1}H-NMR spectrum of a polyhydroxy alkanoate copolymer obtained in Example 11, and including 3-hydroxy-5-(phenylsulfonyl)valeric acid represented by a chemical formula (50), a 3-hydroxy-9-carboxynonanoic acid represented by a chemical formula (45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy--5-carboxyvaleric acid represented by a chemical formula (47).

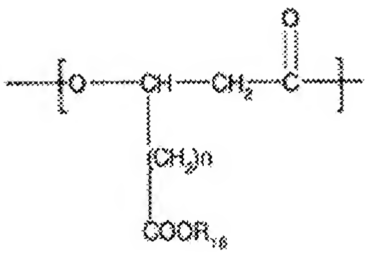
[Name of the Document] Abstract

[Abstract]

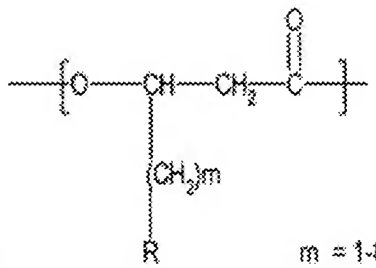
[Problem(s)] It is to provide PHA having an active group and a production method therefor, such that PHA can be produced by a microorganism at a high yield, the unit ratio of the active group can be controlled, and its physical properties can be freely regulated not to limit its application as a polymer.

[Means for Solving the Problem(s)] The invention provides a PHA copolymer including at least a 3-hydroxy-ω-carboxyalkanoic acid represented by a formula (19) and simultaneously at least a unit represented by a formula (2) or a formula (3) in a molecule, a precursor PHA copolymer having a corresponding vinyl group or a corresponding alkoxycarbonyl group, a biosynthesis method thereof by microorganisms, and a method of producing a desired PHA copolymer from the precursor PHA copolymer:

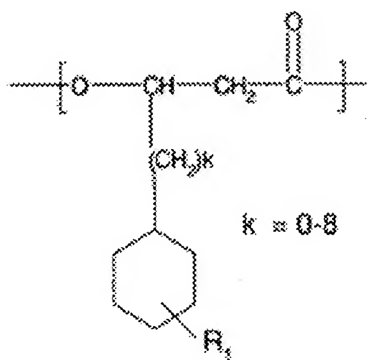
[Chemical Formula 1]



n = 1-8 (19)



m = 1-8 (2)



k = 0-8

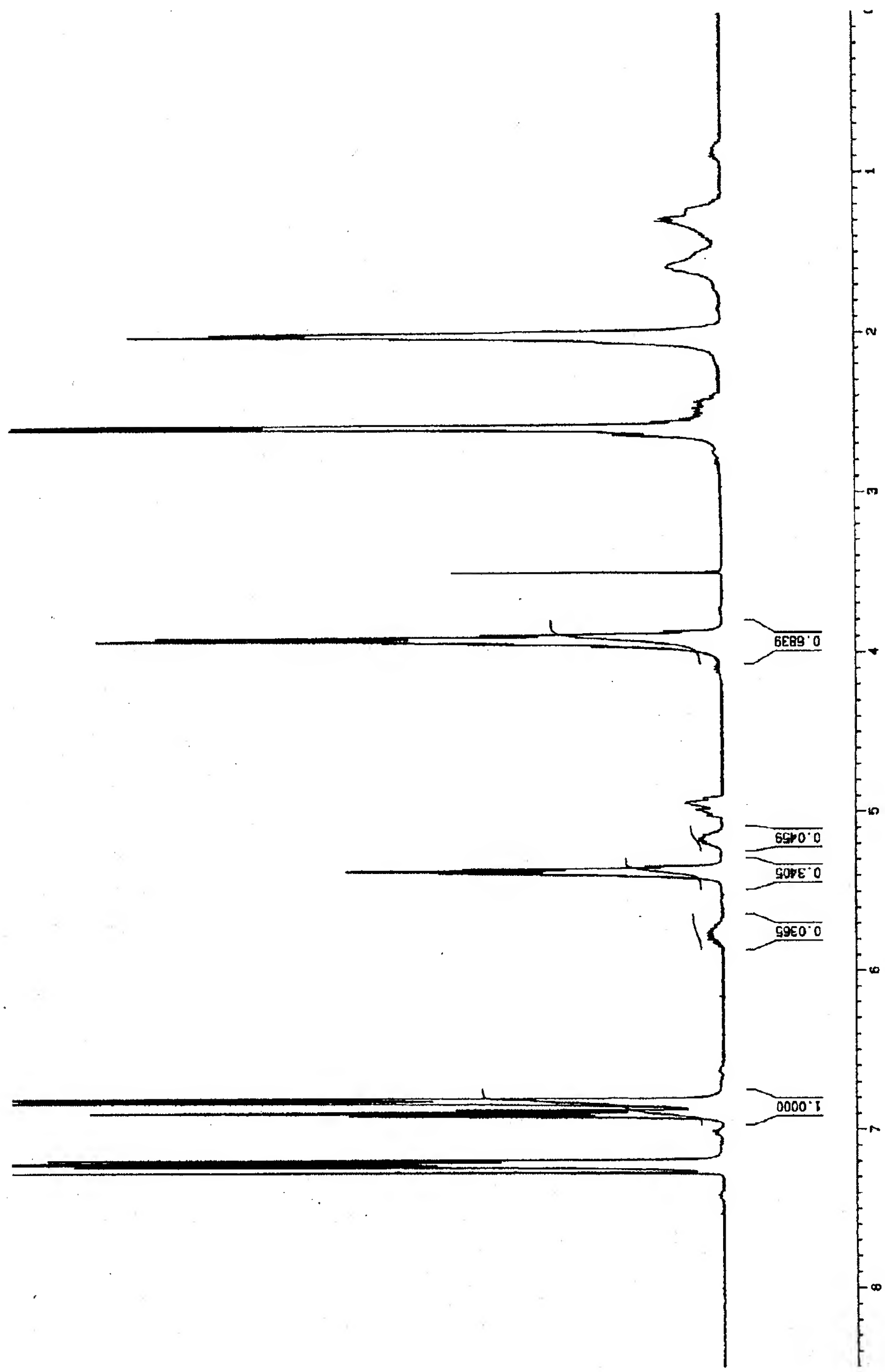
(3)

(wherein k, m, n are integers; R_{18} represents H, Na, K, or; R_1 represents a substituent on a cyclohexyl group and represents H, CN, NO_2, a halogen atom, CH_3, C_2H_5, C_3H_7, CF_3, C_2F_5, or C_3F_7; R includes a residue including a phenyl structure or a thienyl structure; these being independent for each unit).

[Elected Drawing] None

【書類名】　　図面

【図１】



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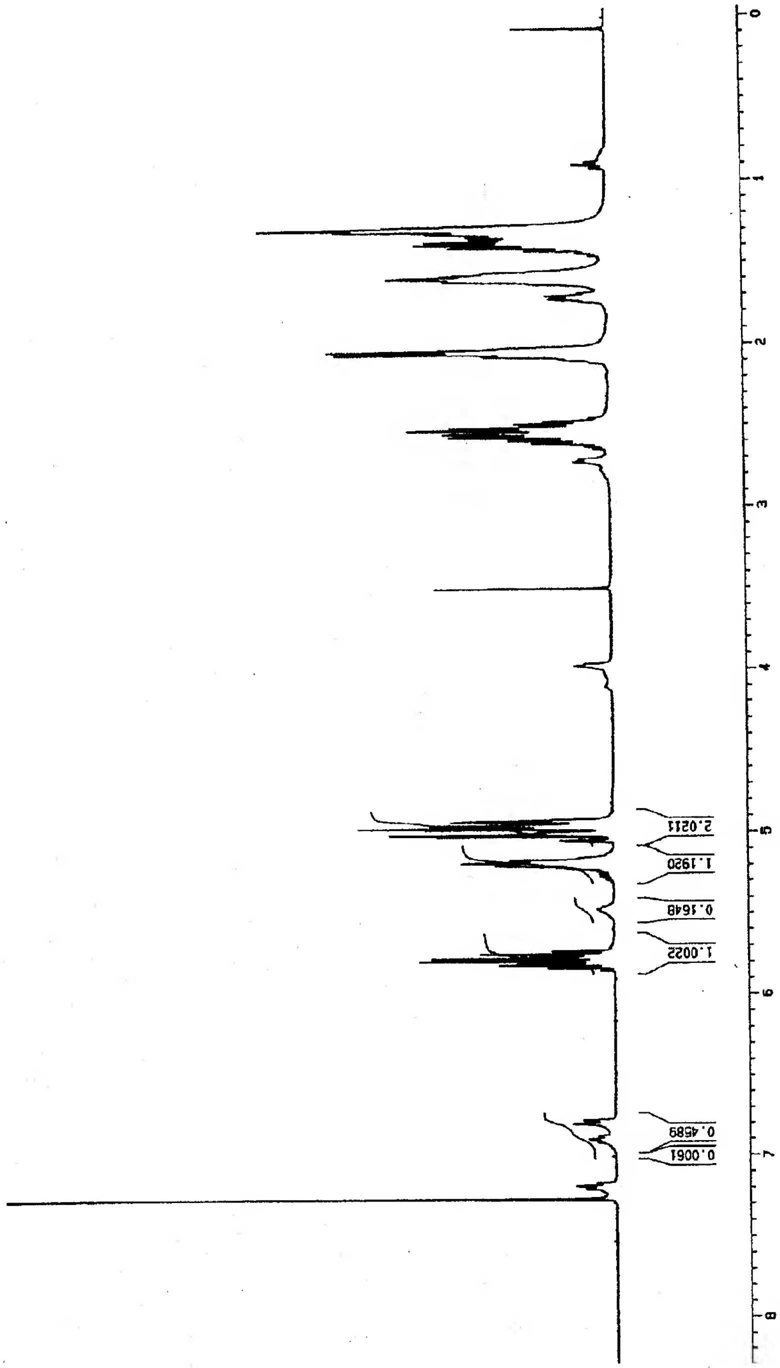

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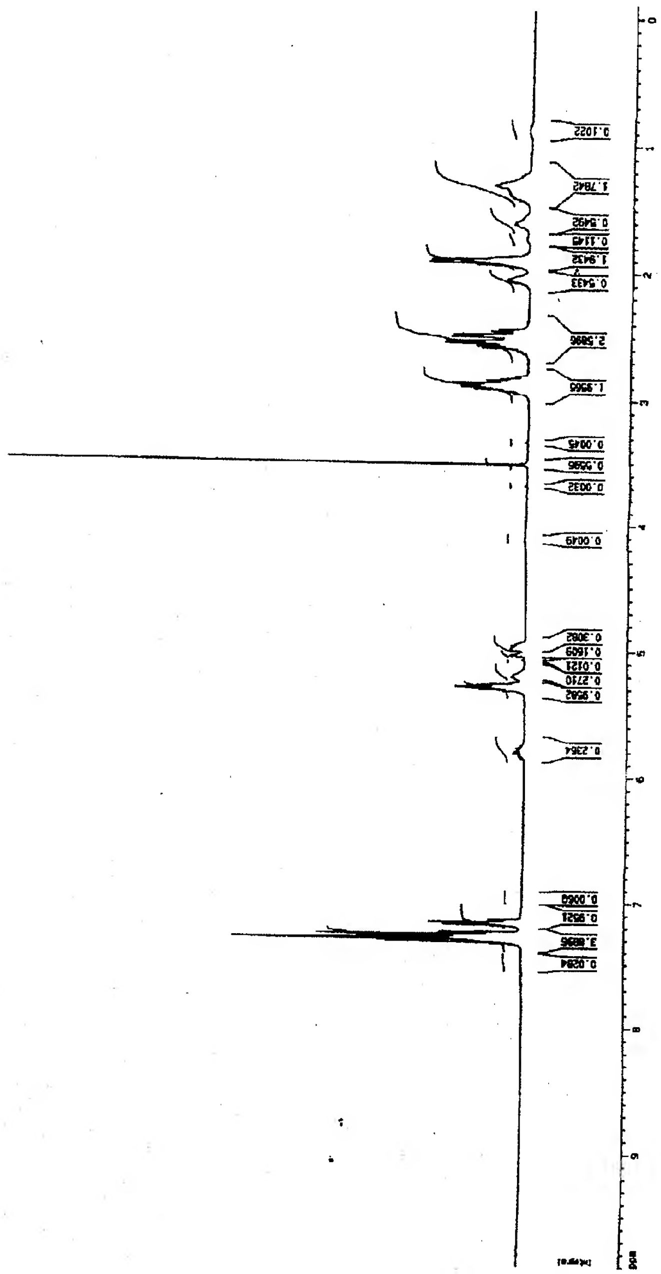

【図４】